ALUM-CATIONIC POLYMER INTERACTIONS IN THE DIRECT FILTRATION OF COLOURED WATERS

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by

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To

Sergio, my husband

Olivete and Joram, my parents

ABSTRACT

Alum-assisted direct filtration is a common process for treating upland, coloured surface waters. Because of the concerns about the effects of both aluminium and trihalomethanes in human health there has been a growing interest in improving the removal of colour from drinking waters whilst maintaining low residual aluminium concentrations. This dissertation describes a laboratory-based study designed to evaluate the effect of the partial replacement of alum by a cationic polyelectrolyte on the performance of direct filtration of coloured waters, and to investigate how cationic polymers act in conjunction with alum in precipitating organic colour.

The experiments were carried out at pH 6 and using a synthetic coloured water at two colour concentrations, prepared from an aquatic humic extracted material. Filtration tests were performed under different pre-treatment conditions, varying from coagulation with alum-only to coagulation with polymer-only, passing through various alum-polymer combinations. Filter performance was assessed, principally, by means of a non-dimensional performance index, the Ives' filterability number.

Floc characteristics were determined for a number of alum-cationic polymer combinations in an attempt to correlate such characteristics with the filtration performance. The floc characteristics investigated were floc size and floc charge.

The results indicate that when alum is used in combination with a cationic polymer to coagulate organic colour, charge neutralization is an important mechanism. The minimum filterability number (optimum filtration performance), for each constant alum dose, occurred at the polymer dose where the net charge of the floc is near zero and coincides, approximately, with the maximum floc size entering the filter. At polymer doses higher than that corresponding to the zero zeta potential of the floc, restabilization was observed and filtration performance deteriorated rapidly. In contrast, satisfactory filtration performances were achieved at polymer doses considerably lower than that corresponding to the minimum filterability number.

In general, the partial replacement of alum by a cationic polymer was shown to increase the duration of the filtration run, but it had a detrimental effect on the quality of the filtered water, both in terms of residual apparent colour and residual aluminium.

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ERRATA

p. 20	line 3	delete "Δ", insert "ΔH"
p. 31	line 8	delete "conciliate", insert "reconciles"
p. 31	line 11	delete "exit", insert "exits"
p. 45	line 8	delete "to", insert "too"
p. 60	line 12	delete "Unican", insert "Unicam"
p. 61	line 9	delete "adsorption", insert "absorption"
p. 65	line 22	delete "indicate", insert "indicates"
p. 75	line 1	delete "adsorption", insert "absorption"
p. 84	line 8	delete "flow", insert "flows"
p. 84	line 18	delete "silicon", insert "silicone"
p. 90	line 5	delete "occurred", insert "occurring"
p. 93	line 10	delete "Unican", insert "Unicam"
p. 93	line 24	delete "$Al_2(SO_4).16H_2O$", insert "$Al_2(SO_4)_3.16H_2O$"
p. 128	line 16	delete "criteria", insert "criterion"

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LIST OF PRINCIPAL SYMBOLS AND ABBREVIATIONS

(Other terms are defined where quoted)

Abs.	Absorbance unit
Al	Aluminium
B.S.	British Standards
$\boldsymbol{C}$	Average filtrate quality
$\boldsymbol{C}_o$	Inlet suspension quality
C	Residual colour of treated water
C_o	True colour of raw water
C_o*	Apparent colour of coagulated water
°C	Degree Celsius
cm	Centimetre
d	Diameter
D	Translational diffusion coefficient in Stokes-Einstein equation
DLS	Dynamic light scattering
DOC	Dissolved organic carbon
E	Electrical potential (Volts)
F	Filterability Number
FA	Fulvic acid
FCS	Photon correlation spectroscopy
FTU	Formazin turbidity unit
g	Gravitational acceleration
G	Average velocity gradient
h	Hour
H	Total head loss through the filter
IR	Infra-red
k	Boltzmann's constant
K_f	Carman-Kozeny constant
l	Litre
L	Length
m	metre
m	Refractive index
mB	Millibar
mg	Milligram
min	Minute
ml	Millilitre

mm	Millimetre
mV	Millivolt
MW	Molecular weight
nm	Nanometre
NMR	Nuclear magnetic resonance
NTU	Nephelometric turbidity unit
PAC	Polyaluminium chloride
PEI	Polyethylenimine
ppm	Parts per million
q	Length of the wave vector
Q	Flow rate
R	Radius
R_H	Hydrodynamic radius
rpm	Revolutions per minute
RO	Reverse osmosis
s	Second
SD	Standard deviation
t	Time
T	Turbidity of treated water
$\mathrm{T_o}$	Turbidity of raw water
$\mathrm{T_o}$*	Turbidity of coagulated water
T_a	Absolute temperature
TC	Total carbon
TOC	Total organic carbon
THM	Trihalomethane
THMFP	Trihalomethane formation potential
TTHM	Total trihalomethane
U	Electrophoretic mobility
UV	Ultra-violet
v	Velocity
V	Volt
V	Volume
V_e	Electrophoretic velocity
Z	Z average diameter

Greek letters

ϵ	Dielectric constant
Δ	Head loss
ζ	Zeta potential
η	Viscosity
Λ	Wavelength
λ	Filtration removal coefficient
µg	Microgram
µm	Micrometre
µS	Micro-Siemens
ν	Kinematic viscosity
τ	Delay time

1. INTRODUCTION

1.1 Importance of colour removal in water treatment practice

Humic substances comprises a general class of biogenic, refractory, yellow-black organic substances that are ubiquitous, occurring in all terrestrial and aquatic environments. These substances constitute the major organic fraction in soil and have been studied by soil scientists for two centuries (Aiken, 1985).

Humic substances are amorphous, acid, hydrophilic, predominantly aromatic and chemically complex polyelectrolytes. There are three major fractions of humic substances defined in terms of their solubilities:

- Humin - Fraction that is not soluble in water at any pH.
- Humic acid - Fraction that is not soluble in water under acid conditions (below pH 2).
- Fulvic acid - Fraction that is soluble in water under all pH conditions.

According to Aiken (1985) these definitions have survived the test of time because of their practical utility. Water solubility is an effective criterion because of its dependence on important chemical characteristics such as functional groups, molecular weight, aromaticity and so on.

Aquatic humic substances constitute 40 to 60 percent of dissolved organic carbon and is the largest fraction of natural organic matter in water. In general, the fulvic acids make up about 85% of the humic substances from rivers and streams, they have a molecular weight of 500 to 2000 and are dissolved rather than colloidal. The humic acid make up the remainder 15% with a molecular weight ranging mainly from 2000 to 5000, but sometimes as large as 100000 (Thurman, 1985). In the pH of most natural waters humic substances are negatively charged (Vik and Eikebrokk, 1989) and the major functional groups are carboxyl, hydroxyl, carbonyl and a lesser amount of phenolic hydroxyl.

Humic substances are responsible for the yellow-brown colour imparted to unpolluted waters containing high organic dissolved matter. Because such substances are thought to be harmless as pure compounds, the removal of colour from drinking water was traditionally due to aesthetic reasons - for most people colour becomes objectionable and unaesthetic at levels over 15 colour units (Faust and Aly, 1983). However, the discovery by Rook (1974), later confirmed by other researchers, that the chlorination of natural waters leads to the formation of haloforms and that humic substances acts as precursors, brought about a reassessment of the importance of colour removal in the water treatment practices.

Among the chlorinated by-products resulting from the chlorination process are the trihalomethanes (THM). Concerns about the potential health risks of these compounds have inspired a number of toxicological studies and surveys and, as a result, a limiting level of 100 µg/l of total THM (TTHM) in drinking waters was set in most developed countries (USA, UK and other EEC countries). The World Health Organization (WHO) does not suggest a guideline value for THM as a whole, instead, a value of 30 µg/l of chloroform is recommended (WHO Guidelines, 1984). Chloroform, one of the most investigated of the THM, has been shown to cause cancer to animals and is regarded as a potential cancer risk in human.

The avoidance of THM in drinking waters has been approached by scientists in two alternative ways: (1) remove the THM after their formation or (2) prevent the formation by either changing the disinfectant to non-chlorine products or removing the precursors before the chlorination step.

Besides the potential formation of THM, other reasons for removing colour/humic substances from potential water supplies currently cited in the literature (Narkis and Rebhun, 1977; AWWA Research Committee on Coagulation, 1970, 1979; Vik et al., 1985) are:

- Humic substances have the ability to form stable complexes with heavy metals and adsorb pesticides and insecticides, acting as a vehicle for these pollutants transport and/or making difficult their removal in the water treatment;

- Interference in other phases of the water treatment process like oxidation and removal of iron and manganese, demineralization by fouling anion exchange resins or membranes and others;
- Increasing in the chlorine demand during disinfection.

The partial removal of organic matter (humic substances/THM precursors) from drinking waters can be achieved (i) through coagulation followed by a suitable separation process, (ii) by adsorption on activated carbon, (iii) by the use of membrane processes (reverse osmosis and ultrafiltration), (iv) by chemical oxidation, (v) by precipitative softening and other processes. The most popular and cost effective processes among them are coagulation and activated carbon.

According to Kavanaugh (1978), although coagulation may not be as effective as activated carbon in achieving the required organic reduction to allow chlorination and meet the THM standards, coagulation still has advantages over activated carbon - such as: little or no required capital investment and minimal increase in unit operating cost - that supports the idea that an 'improved' coagulation deserves consideration as a method for reducing THM precursors level. Within this philosophy the coagulation of humic substances has been the objective of various works, and a great deal of achievement has been reported.

1.2 Colour removal by coagulation

Many studies on the coagulation of coloured waters have been conducted since the 1960s. Whereas some of these studies focused their attention to specific aspects of colour removal, such as:

Reduction of THM formation potential;

Minimization of the residual coagulant concentration;

Relation between coagulant efficiency and characteristics of the water being treated; etc,

a number of other investigations were devoted to the understanding of the mechanisms involved in the coagulation of humic substances. The studies summarized in the two following sections give some examples of the aspects covered in the literature but it does not intend to be a complete review.

1.2.1 General aspects of colour removal

Packham (1973) in an extensive experimental survey evaluated, by means of jar tests, the ability of 24 cationic polymers in precipitating fulvic acid extracted from The River Thames. The maximum removal obtained with the various polymers ranged widely from 3 to 87% with doses between 2-16 mg/l being applied. The flocs formed were reported to be very small and settled very slowly, giving the treated water unacceptably high turbidity. The addition of clay prior to coagulation brought about a considerable improvement in colour removal probably due to an increase in the rate of flocculation. The ability of a specific polymer to precipitate fulvic acid was shown to increase with the degree of cationic substitution but was much less affected by differences in molecular weight.

Comparing the use of some of these polymers with alum for three natural waters, Packham showed that in all cases alum was more efficient than the polymers in removing both colour and turbidity, although in some situations differences were small.

In a similar way, Edzwald and co-workers (Edzwald et al., 1977; Edzwald, 1979) conducted studies on the coagulation of humic and fulvic acids by various polymers of different charge type (cationic, anionic and nonionic polymers) and different molecular weight, where the polymer was either used as sole coagulant or in combination with alum. As in Packham's work, it was observed that cationic polyelectrolytes, when used as sole coagulant, can successfully interact with humic and fulvic acids but the flocs formed were not settleable. They disagree, however, on the effect of molecular weight, finding better colour removals with cationic polymer of high molecular weight. Under the conditions studied both alum and cationic polymer exhibited stoichiometry between humic concentration and optimum dose of coagulant.

Little or no removal was observed when either the anionic polymer or nonionic polymer was used as primary coagulant. Alum combined with polymers was shown to perform better than the respective polymers alone, particularly when high molecular weight polymers were used. The best combination was alum-nonionic polymer which, at the optimum combination, led to the formation of settleable flocs. Restabilization due to overdosing was observed whenever polymer was used.

Babcock and Singer (1979) investigated the extent to which the removal of colour (humic and fulvic acid fractions) by alum coagulation influences the reduction of chloroform formation and total organic carbon (TOC). The results of the coagulation tests showed that, although colour and TOC removal follow a parallel pattern with the increase of the alum dosage, the extent of colour removal is considerable higher than TOC removal, particularly for fulvic acid solutions (see figure 1.1). Moreover, coagulation at the optimum alum dose led to appreciable reductions in both colour and formation of chloroform while only relatively small reductions in TOC were observed, suggesting that coagulation of humic and fulvic acids by alum results in a selective removal of those portions of humic and fulvic acids most responsible for colour and for chloroform production.

It was also clear that the coagulation of fulvic acid is less effective than humic acid with high alum doses being necessary to achieve similar degree of removal.

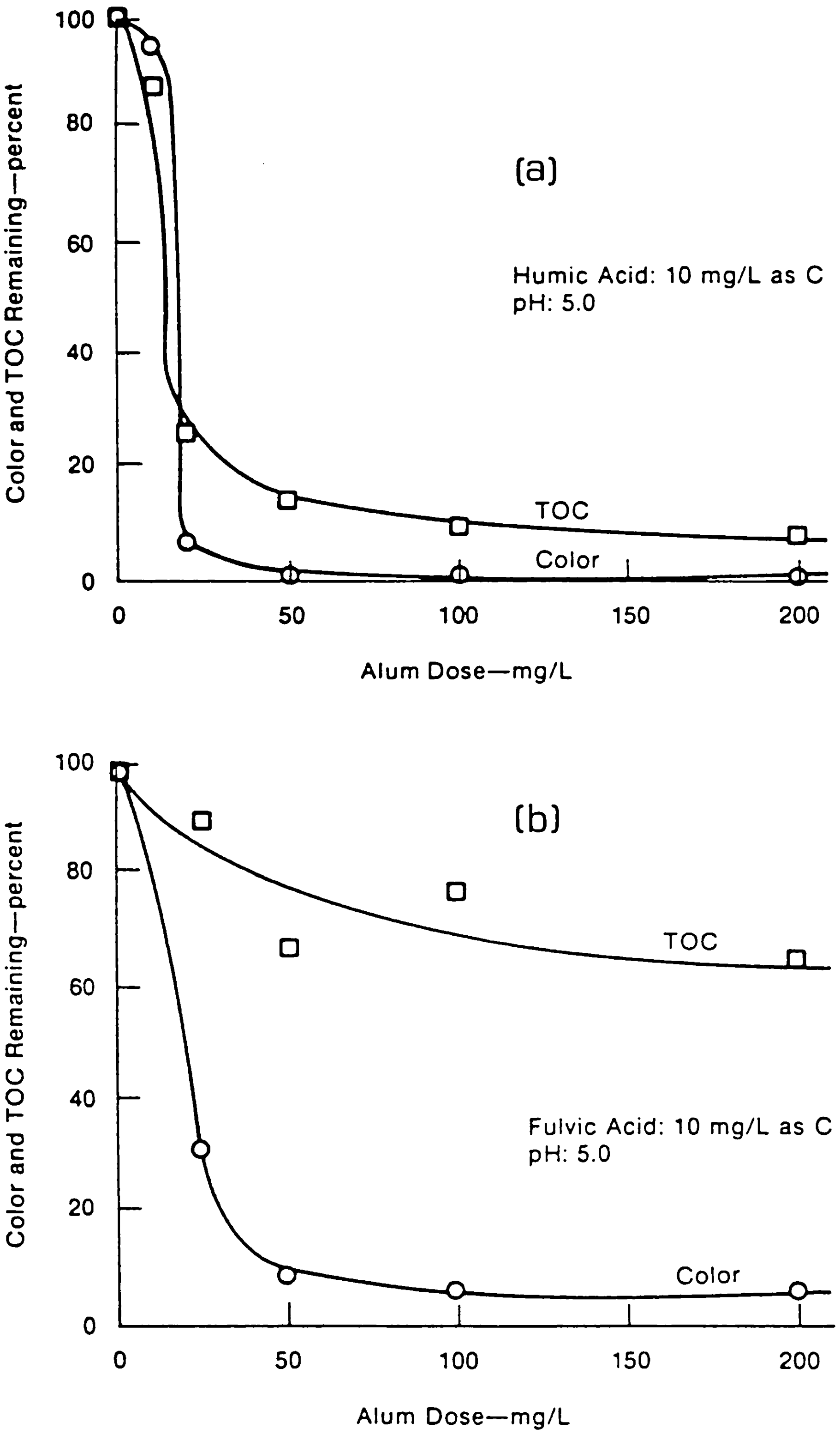


Figure 1.1: Effect of alum coagulation on colour and TOC removal from (a) humic and (b) fulvic acid solutions (after Babcock and Singer, 1979)

The effect of differences in raw water characteristics on the coagulation of humic substances (THM precursors) was studied by Amy and Chadik. In their investigation they coagulated various synthetic and natural high coloured waters with a number of different cationic polyelectrolytes (Amy and Chadik, 1983) as well as two metal coagulants (Chadik and Amy, 1983). The major parameter analyzed was the THM formation potential (THMFP).

The maximum reduction in THM formation potential obtained for the synthetic waters varied from 0 to 92% depending on the type of polymer and water tested (humic or fulvic solution with or without kaolinite). As observed by Babcock and Singer (1979) for alum coagulation, the various polymers were significantly more effective in coagulating the humic acids than the fulvic acids. The easier coagulation of the humic acids is attributed to the lower charge density of this fraction in comparison to the fulvic acids. During the coagulation tests the formation of a settleable floc was never observed, instead a colloidal precipitate that proved to be stable and remained in suspension was produced. This colloidal precipitate was however effectively removed by filtration through a 0.45 micron filter. The presence of kaolinite was shown to enhance the coagulation. Both observations are in agreement with previous works with cationic polymers as sole coagulant (Packham, Edzwald etc).

For the natural waters the effectiveness of polymer coagulation varied dramatically as a function of both polymer and raw water source, with maximum reductions in THMFP ranging from 26 to 65%. The best results were observed in waters with low ambient pH levels. Also, the waters with low turbidity were more amenable to polymer coagulation than either those with moderate to high turbidity, or with virtually no clay turbidity. The performance of the two metal coagulants (Alum and Ferric Chloride) were comparable to those achieved with polymers. At natural pH values the alum coagulation was more effective for the same waters (low turbidity) as the polymer coagulants. The use of pH 6 (generally a lower value than the natural pH of the water sources) in the coagulation tests resulted in a marked improvement in THMFP removal for most of waters, especially those with no turbidity.

In another study, where both natural and reconstituted Mississippi River water were used, Semmens and Field (1980) analyzed the effect of some operational parameters in the coagulation of organic matter. The results indicated that the most important variables influencing organic removal by alum coagulation are the alum dose and pH. They found that the flocculation time, order of addition of coagulant/pH correction, sludge recycle and multistage coagulation did not significantly affect organic removal performance. At optimum pH (found to be around pH 5) and high alum doses, organic removals were greater than 50% as TOC and as high as 90% as UV absorbance (colour).

A coagulation study with the main objective of comparing the treatability of natural coloured water from three different sources in England was conducted by Jackson et al. (1988). For each water the effectiveness of coagulation with hydrolysing salts of aluminium and iron was evaluated not only by the removal of colour but also by the removal of iron, aluminium and manganese. From the treatability data obtained the optimum conditions for maximum removal of each parameter was determined. Thus, an overall optimum condition was established such that the coagulation minimised or reduced to acceptable levels all the target parameters (colour, iron, aluminium and manganese).

The optimum overall pH varied slightly for each of the three water sources, but a general trend was observed. Whereas the pH for maximum colour removal depends on the applied coagulant dose, the pH for minimum residual coagulant is not affected by either coagulant dose or raw water colour. The pH for minimum residual coagulant concentration was found to be higher than that for colour removal, however, as coagulant dose is increased, the pH for maximum colour removal tends towards the pH for minimum residual coagulant. Also, the higher the dose of coagulant, the broader the pH range over which colour is removed and higher the pH for maximum removal.

The broadening of the pH range for effective colour removal with the increase of coagulant dose and the differences in the values of the optimum pH with respect to colour removal and residual aluminium were previously observed by Vik et al. (1985) for the alum coagulation of waters from three Norwegian lakes.

1.2.2 The mechanisms of colour coagulation

Aluminium sulphate and other hydrolysing coagulants

Aluminium sulphate is the single most commonly used coagulant for water treatments in the United States, England and various other countries. Other salts of aluminium and iron are also widely used. Among the first to discuss the mechanisms of colour (humic substances) coagulation by hydrolysing salts of aluminium and iron were Black and co-workers in USA and Packham and co-workers in England.

Black and Willems (1961) studied the coagulation of two natural high coloured waters with alum and ferric sulphate by measuring the electrophoretic mobility of the flocs formed. They found that, with regard to the two waters used, the pH range for optimal coagulation was between about 5 and 6 for alum, and between 3.5 and 4.5 for ferric sulphate. Within this pH range of good coagulation the zeta potential, whether negative or positive, was quite low. Based on their experimental results they suggested that the hydrolysis species of the metal salts were responsible for the coagulation of colour (negatively charged organic colloids coagulated by positively charged hydrolysis products) with the trivalent aluminium and ferric ions playing a relatively unimportant role in the overall process.

Hall and Packham (1965) also used inorganic salts of aluminium and iron to study the coagulation of organic colour in synthetic waters prepared with humic and fulvic acid isolated from the River Thames. They found that the optimum pH range for colour removal from these synthetic waters coincide with the range observed by Black and Willems, i.e. about pH 5-6 when alum was used and pH 3.5-4.5 for ferric chloride. The fact that these pH values were lower than that for the coagulation of clay suspensions was regarded as an indication that organic colour and turbidity are removed by different mechanisms.

They proposed that in the coagulation of coloured waters by alum the humic substances are primarily removed by precipitation of an insoluble basic humate or fulvate as a result of the interaction of partially hydrolysed aluminium ions and carboxyl groups on the humic molecules. Such a mechanism is supported by the observed stoichiometric relation between coagulant dose and concentration of humic material. The increase in coagulant doses required at pH values above 5 was thought to be caused by chelation of aluminium by a second type of acidic group on the organic molecule. It was postulated that colour removal mechanisms by iron and aluminium were similar.

The importance of the hydrolysed aluminium species in the coagulation of humic acid and their dependence on pH is emphasized in the work of Mangravite et al. (1975). In this work the stability of humic acid sols as a function of aluminium concentration and pH was studied and as a result, an aluminium-pH domain diagram for two concentrations of humic acid, 5 and 50 mg/l, was established. Two aluminium salts were used, alum and aluminium nitrate.

Two regions of destabilization were identified depending on pH and aluminium dosage. Generally speaking, one region occurs at higher aluminium doses and pH values above 5 where the coagulation of humic acid is accomplished by the presence of aluminium hydroxide precipitate. The other occurs at lower dosages and lower pH values where the humic acids were considered to be destabilized by soluble hydrolysed polynuclear aluminium species. Between the two destabilization regions a restabilization zone was observed. It is believed that in this zone the original humic sols are aggregated, but are stable due to a charge reversal effect resulting from the adsorption of highly charged aluminium species. The presence of sulphate ions in this area can change the position of the area boundaries by coagulation of the positive sol formed.

Edzwald (1979) highlighted the effect of the pH in the coagulation of colour by alum by showing that at higher pH values higher doses of alum were necessary to coagulate the same amount of humic material (figure 1.2). At pH 6 he observed a defined stoichiometry between alum dose and humic acid concentration. In this study Edzwald suggests a model that conciliate some of Mangravite and Packham ideas about the mechanism of colour coagulation by alum. According to the proposed model destabilization of humics by alum may be accomplished by charge neutralization over a pH 4-6, and at these conditions stoichiometry exist between humic concentration and optimum alum dose. At high doses though, precipitation may also be involved where humic material is incorporated within aluminium hydroxide floc or co-precipitated as aluminium humate.

The differences in the mechanism of colour coagulation resulting from the use of three different aluminium salts, namely alum, aluminium chloride and polyaluminium chloride (PAC), is discussed by Dempsey and co-workers (1984, 1985). According to Dempsey the type of aluminium coagulant has a very strong effect on the conditions (pH and aluminium concentration) required for fulvic acid (FA) removal, as well as on the extent of the removal. In terms of fulvic acid removal, the use of alum appears to be preferable within the aluminium-pH domain where precipitation of aluminium hydroxide occurs (sweep floc zone), whereas the PAC seems to be a better coagulant at pH values more acidic and more basic than that corresponding to the alum sweep floc zone. The reactions between fulvic acid and alum or aluminium chloride were broadly classified within three pH ranges: at pH<5 removal may occur by the direct precipitation of fulvic acid by polymeric and even monomeric species of aluminium; between pH 5 and 6 the predominating reaction depends on the applied dosage of aluminium, such that at low doses the fulvic acid will be precipitated by polymers of aluminium; at pH>7 precipitation occurs by adsorption of fulvic acid or soluble

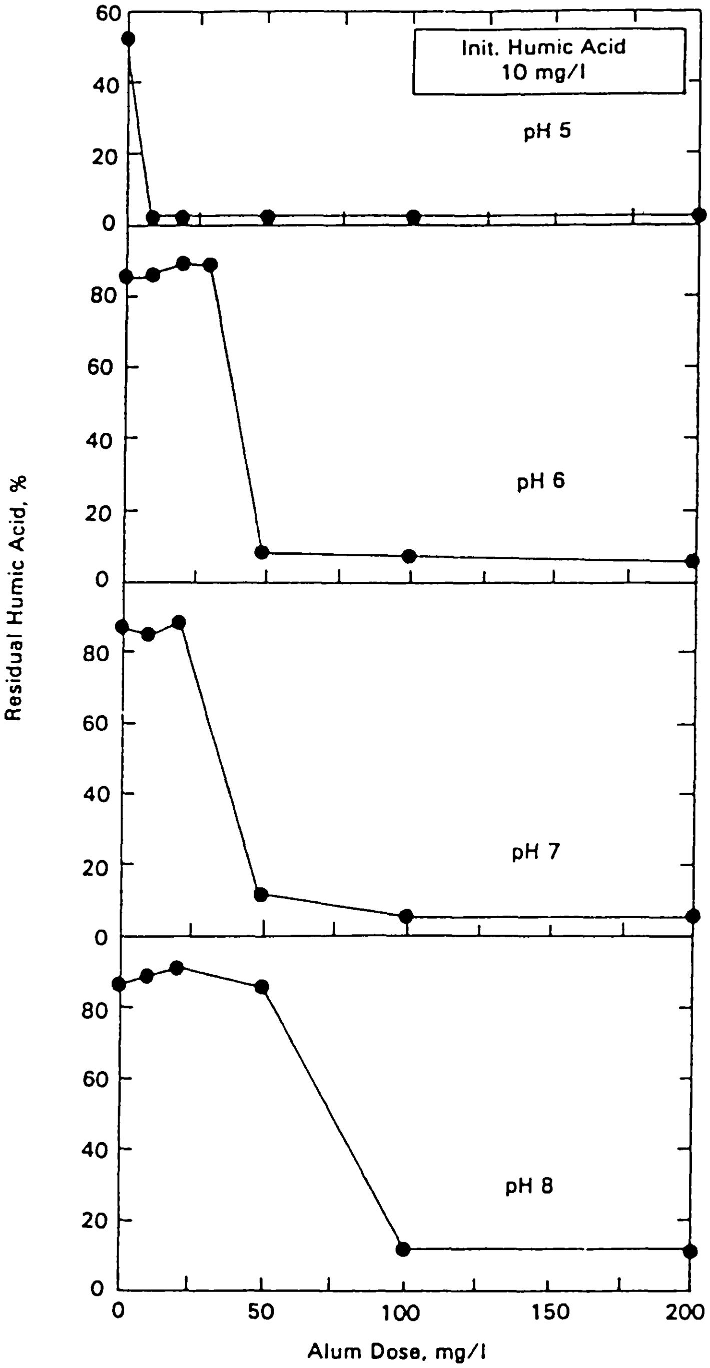


Figure 1.2: Effect of pH in the coagulation of humic acid with alum (after Edzwald, 1979)

FA-aluminium complex on a precipitated aluminium hydroxide. The PAC, due its polymeric nature, directly precipitates fulvic acid over a broad pH range, and this reaction can be defined as charge neutralization since stoichiometry and overdosing occurs.

The difference in mechanisms resulting from the use of different aluminium-type coagulants is elucidated in the work of Hundt and O'Melia (1988). They have shown that the speciation of alum, aluminium chloride and polyaluminium chloride over a wide pH range leads to different Al species distribution which in turn determines the predominant mechanism of fulvic acid removal. In the presence of aluminium monomers and polymers charge neutralization will be the predominant mechanism of FA removal, whereas adsorption will take place whenever aluminium hydroxide has precipitated from the solution. If there is no predominant aluminium species, concurrent reaction by both mechanisms appears to cause simultaneous precipitation.

Dempsey et al. (1984) also found that as the concentration of fulvic acid is increased the amount of coagulant required for coagulation also increases. This increase however may not be linearly proportional to the increase in the fulvic acid concentration, depending upon the type of aluminium coagulant and the mechanism involved.

Edwards and Amirtharajah (1985) determined, based on jar tests, the common colour removal domain for the alum coagulation of a wide range of humic acid concentrations (4 to 37.5 mg/l). Analyzing the results with respect to the 'Design and operation diagram for alum coagulation' previously developed by Amirtharajah and Mills (1982), they found that the removal areas for humic acid involve pH and alum doses similar to those for the removal of turbidity. As can be seen in figure 1.3a, for a humic acid concentration of 4 mg/l one area occurs within the pH range of 4 to 5 and alum doses between 10 and 65 mg/l, where charge neutralization occurs and may result in the formation of an aluminium humate precipitate. This mechanism was substantiated by electrophoretic mobility data acquired. The second area of removal occurs in the region of accelerated precipitation of aluminium hydroxide

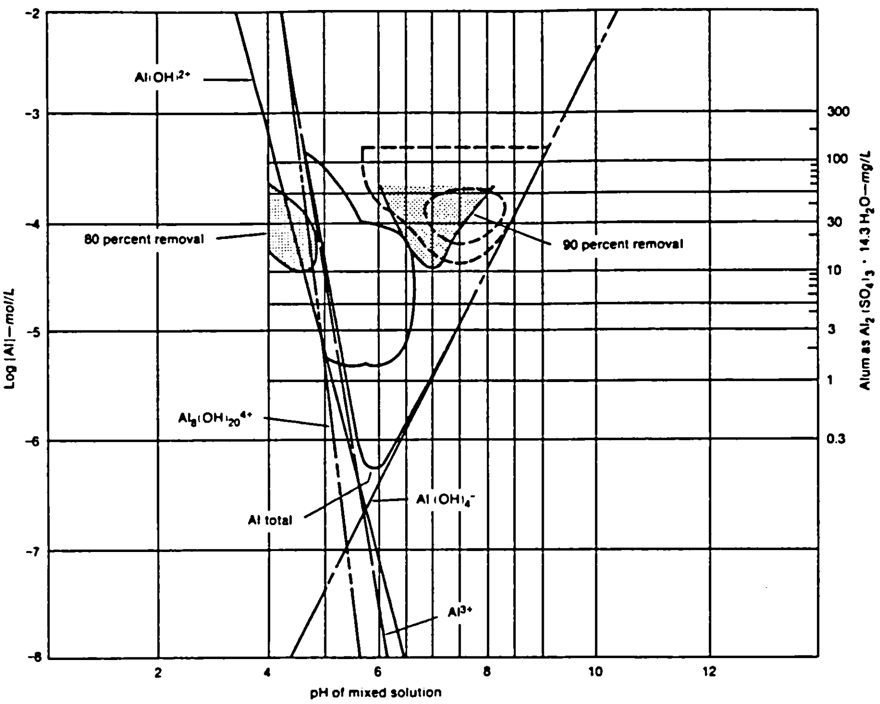


Figure 1.3a: Colour removal domains - 4 mg/l humic acid (100cu), no turbidity (after Edwards and Amirtharajah, 1985)

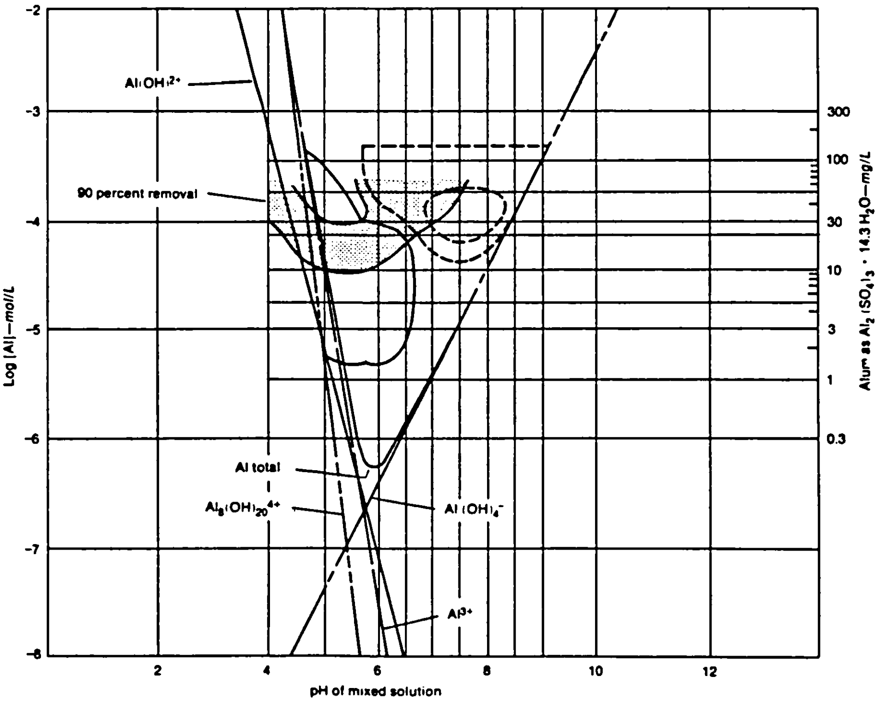


Figure 1.3b: Colour removal domains - 20 mg/l humic acid (450cu), no turbidity (after Edwards and Amirtharajah, 1985)

(pH range of 6 to 8 and alum doses higher than 12 mg/l) where removal is probably associated with adsorption on the aluminium hydroxide floc. This region corresponds to sweep coagulation for removal of turbidity. For high humic acid concentrations the two areas connect to form a single removal band (e.g. figure 1.3b). The authors concluded that the mechanisms involved in the removal of colour by alum appears to be closely related to those for the removal of turbidity.

Vik et al. (1985) have shown that in the coagulation highly coloured waters (TOC concentrations varying from 6 to 15 mg of C/l) from three Norwegian lakes by alum the efficiency of removal was dependent of the precipitation of aluminium hydroxide. The residual aluminium concentrations followed the equations for solubility of aluminium hydroxide with respect to Al^{3+} and $Al(OH)_4^-$, that suggests that no other hydrolysis species were involved in the process. It is suggested that charge neutralization would probably be a important mechanism if the raw water contained less organic material.

From the studies previously described it is clear that the coagulation of colour (humic substances) by aluminium salts (and probably salts of iron) can be achieved by two mechanisms (i) charge neutralization and (ii) adsorption on precipitated aluminium hydroxide. These two mechanisms have distinct differences from their turbidity counterparts. In the charge neutralization for turbidity removal destabilization is brought about by adsorption of the aluminium hydrolysis products on the surface of the particles resulting in a reduction of the repulsive potential, whereas for colour removal charge neutralization is thought to occur via reaction between the cationic species of aluminium and anionic humic substances resulting in the formation of a humate precipitate. In the second mechanism, the colour appears to be adsorbed on the aluminium hydroxide precipitate while turbidity is physical entrapped by the precipitated aluminium hydroxide (sweep coagulation).

The predominance of each mechanism seems to be mainly dependent on the aluminium dose applied and the pH under which coagulation takes place. The precise boundaries of the domain (pH and aluminium dose ranges) of each of the two mechanisms is a function of both type of aluminium salt used and characteristics of the water being treated, including presence of sulphate ions, alkalinity, ionic strength, humic substances origin, etc. Under some circumstances both mechanisms can act simultaneously.

Organic polyelectrolytes

The use of polyelectrolytes, mainly those positively charged, as sole coagulant or coagulant aid has been suggested as an option to improve colour removal. Some advantages in using polyelectrolytes have been claimed, among them the fact that polymers tend to form strong and compact flocs. However, very few of the studies about the coagulation-flocculation by organic polymers that have been published specifically deal with the aspect of colour coagulation.

According to Gregory (1985) polymeric flocculants operate by a variety of mechanisms such as bridging, charge neutralization (including electrostatic patch effects), complex formation and depletion flocculation. Only the first two are regarded as important in the water treatment field. In bridging flocculation polymer segments are 'simultaneously' adsorbed on the surface of adjacent particles thereby binding them together while in the charge neutralization polymers, carrying charge of opposite sign of charge to the particles, are adsorbed on the particles in a flat configuration reducing the potential energy of repulsion between adjacent particles (Bratby, 1980).

Narkis and Rebhun (1975), when investigating the flocculation of clay suspension in the presence of humic substances by using a cationic polymer with molecular weight 330000, found that the destabilization of salts of humic and fulvic acids was essentially the result of charge neutralization, with bridging leading to flocculation. Determination of the residual quantities of humate and fulvate after coagulation showed that maximum turbidity of the coagulated suspension is produced at precisely the optimum dose for the precipitation of the humic material. This dose was observed to be slightly lower than that corresponding to the isoelectric point. At the isoelectric point optimum flocculation was reached.

When the cationic polyelectrolyte was added to either a mineral clay suspension or to an organic-clay complex suspension dispersed in humic or fulvic acid solution, colloids and organic matter competed for reaction with the polymer. The organic acids were found to react first and only after the complete reaction with the organic matter did the flocculation of clay begin.

In a later study, where a polyelectrolyte of lower molecular weight (30000) was used, Narkis and Rebhun (1977) confirmed the above findings and postulated a stoichiometric relationship between concentration of the anionic groups associated with the humic matter and polymer demand. They also observed that the reactions of flocculation (coagulation) were sensitive to the pH of the solution with better results at lower pH. A decrease in pH leads to a decrease in the degree of dissociation of the organic molecules of humic and fulvic acid, reducing consequently the coagulant demand. In addition, the reduction in the degree of dissociation leads to lower solubility, thereby increasing the hydrophobic character of the humic molecules and increasing its tendency to leave the solution.

Glaser and Edzwald (1979) reported on the coagulation of humic acids using a homologous series of cationic polyelectrolytes. A stoichiometry was observed between the raw water humic acid concentration and the optimum polymer dose for destabilization. They suggested a model for destabilization and aggregation of humic acids by cationic polyelectrolytes that is illustrated in figure 1.4. In the model proposed they agree with Narkis and Rebhun (1975, 1977) about the mechanism of destabilization but disagree about how aggregation takes place. According to the model (figure 1.4) destabilization of the humic matter is accomplished by charge neutralization and aggregation occurs when the destabilized particles cross-link via specific charged sites, a sort of electrostatic patch effect.

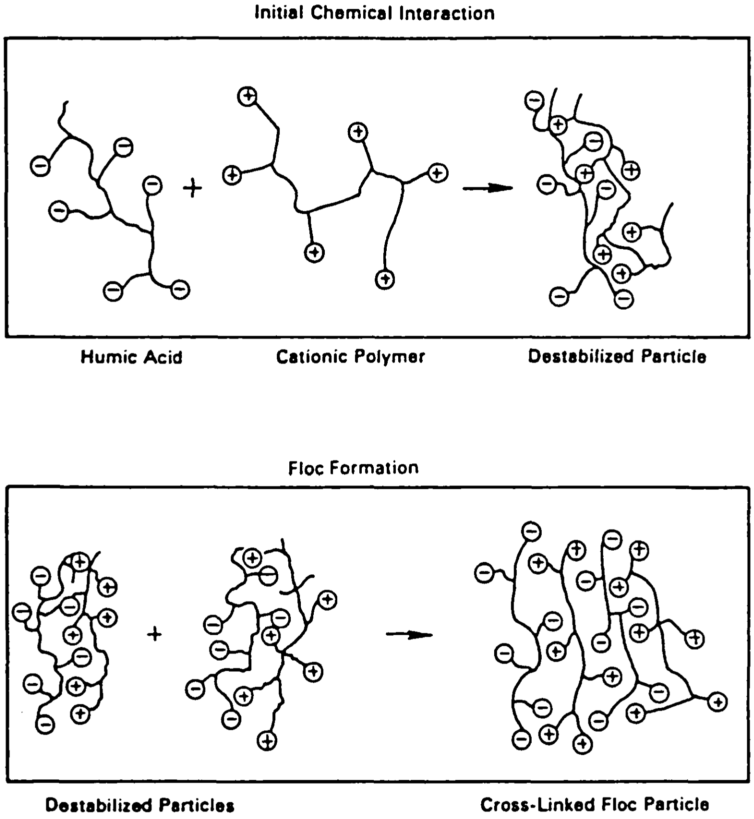


Figure 1.4: Schematic representation of destabilization and aggregation of humic acid by cationic polyelectrolyte (after Glaser and Edzwald, 1979)

A common picture observed in most of the studies that report on the use of polymer as sole coagulant for the removal of colour is the fact that the flocs formed are not settleable. Instead, coagulation produces a colloidal solution characterized by a high turbidity that remains in suspension after a designated period of settling. However, these sols are reported to be effectively removed by subsequent filtration through filter papers or centrifugation. This characteristic behaviour of coloured waters coagulated by polymers was reported, among others, by Packham (1973), Narkis and Rebhun (1975, 1977), Edzwald and co-workers (1977, 1979) and Amy and Chadik (1983).

The use of alum-polymer combinations to coagulate colour was studied by Edzwald et al. (1977). They reported an improvement in colour removal (cf. alum and polymer alone) when alum is used in combination with any of the polymers tested (cationic, anionic and nonionic polymers). In all cases, overdosing with polymer was shown to result in restabilization. They postulated that the destabilization mechanisms for alum-polymer coagulation of humic acid under the conditions tested (low alum dosages at acidic pH) include the adsorption-charge neutralization by soluble hydrolysed aluminium species and inter-particle bridging by high molecular weight polymer.

1.3 Direct filtration and colour removal

Direct filtration is a water treatment scheme where all particulate material - both the naturally occurring and those added or precipitated in the pretreatment steps - is removed in the filter, thereby differing from the conventional filtration train by the lack of a sedimentation tank. Direct filtration schemes may or may not include a flocculation step and when no flocculation time is provided it is frequently called 'in-line' or 'contact filtration'. These filtration configurations are shown schematically in figure 1.5.

Because all suspended matter has to be removed in the filter, the amount of solids present in the water is usually a constraint to the use of direct filtration. The determination of the precise boundaries and operational limits of the various filtration modes has been the subject of a number of studies. According to the AWWA Filtration Committee (1980) natural waters with low turbidity and colour proved to be the most suitable for direct filtration, with colour exceeding 30-40 Hazen (Pt/Co) units or turbidity higher than 15 FTU on a continuing basis being reported as expected to give problems.

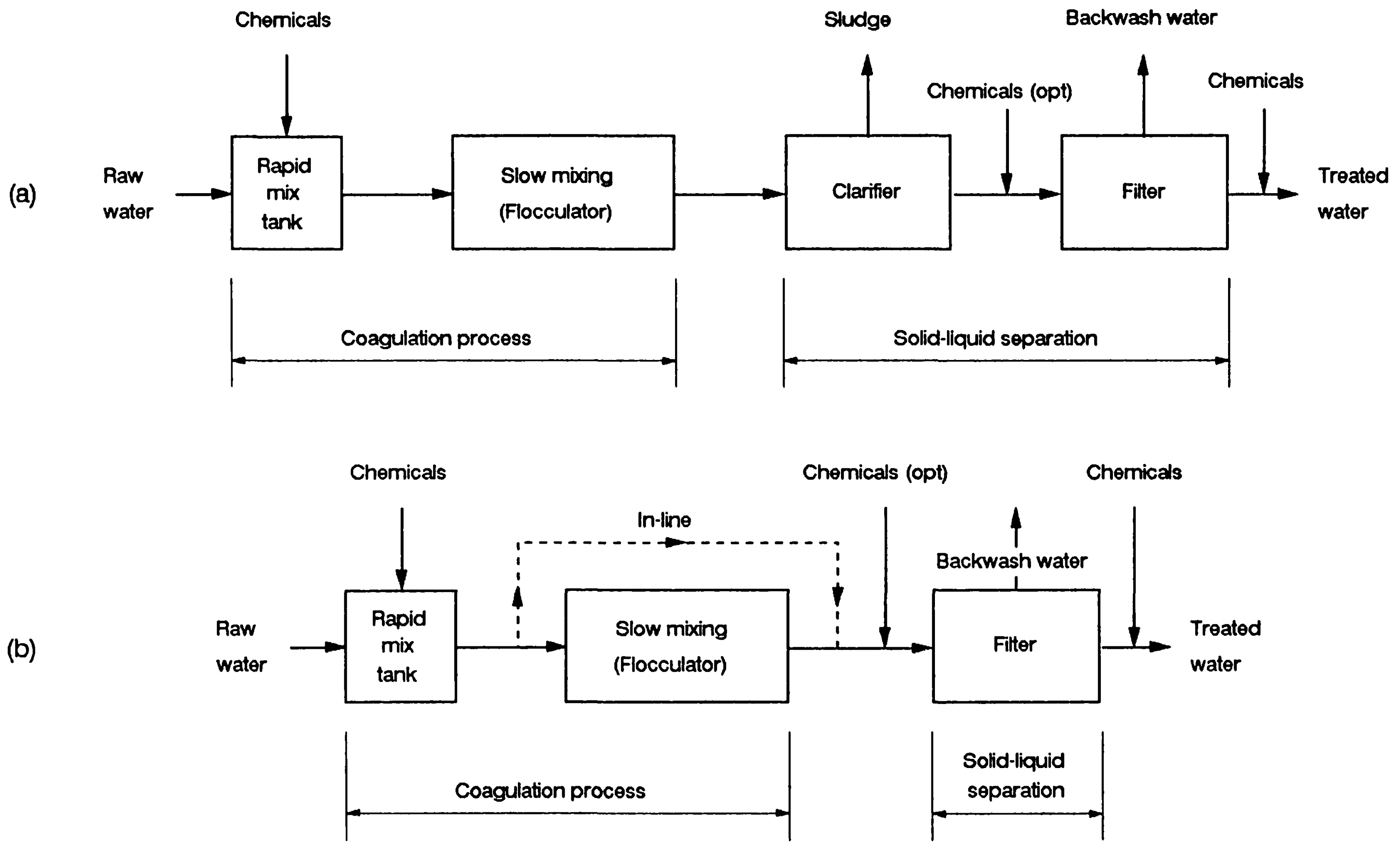


Figure 1.5: Flowsheets for (a) typical conventional filter plant and (b) typical direct filtration plant (after Edzwald, 1982)

Wagner and Hudson (1982) suggest a rough criterion, based on simple jar test and filtration through filter paper, to evaluate the potential use of direct filtration for a specific water. "If the coagulant dose that is required to obtain low turbidity or colour is high (>20 mg/l) economical filter performance is doubtful. Filter clogging is related directly to the floc volume that is loaded onto the filter, and floc volume is related directly to coagulant dose. Therefore, low coagulant doses increases the chances of a successful treatment by direct filtration".

A more elaborated criterion is the use of Wiesner's optimal configuration diagram shown in figure 1.6 (Wiesner et al., 1987). The regions where contact filtration, direct filtration and conventional treatment dominate with respect to the minimization of costs are presented as a function of mass concentration and particle size. The diagram is a result of a combined simulation/optimization approach where physico-chemical models of the processes involved were used as constraints in a least cost formulation, optimized for different conditions of particle concentration and size in the raw water.

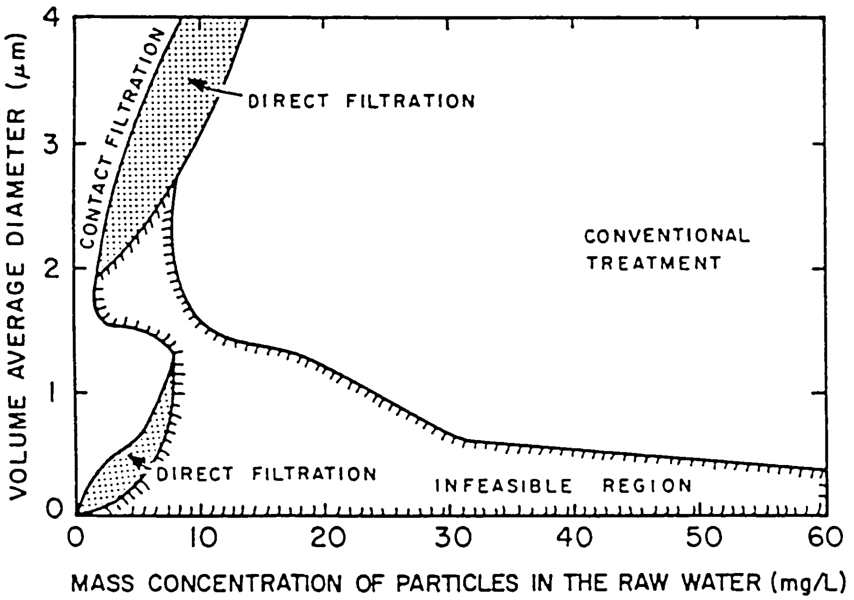


Figure 1.6: Optimal water treatment configuration as function of raw water characteristics (after Wiesner et al., 1987)

Because the model assumes that coagulant addition does not contribute significantly to particle volume, considering total particle volume after rapid mixing equal to the original particle volume in the raw water, in practice it is only valid for raw waters with very low dissolved organic matter and when polymers are used as the coagulant. So, for waters with high colour (high DOC) it may be necessary to introduce a correction for particles created (precipitated) or added during the pretreatment. As an approximation, it has been suggested that at least 1.6 ppm of particle volume per mg of DOC/l should be added to the measured particle volume concentration in the raw water when estimating the final particle volume to be treated after coagulant addition (Wiesner and Mazounie, 1989).

Whatever the criteria, they might be used as a guidance, with the objective to minimize and complement pilot plant work and not substitute it. The criteria may help to identify the ineffective processes or less sensitive variables reducing then the amount of pilot scale tests.

The use of direct filtration for removing turbidity from low turbidity waters is widely reported in the literature with its effectiveness and attractive low costs always emphasized. In contrast, very little is reported about direct filtration of coloured waters, particularly those with moderate to high colour concentrations. Most of the investigations related to the use of direct filtration to remove organic matter has been carried out by Edzwald and co-workers in the USA.

Very good removal of colour from synthetic (humic acid solution) and natural coloured waters by direct filtration are reported by Glaser and Edzwald (1979), using a series of polyethylenimine (PEI) polymer with molecular weight ranging from 600 to 50000-100000, and by Scheuch and Edzwald (1981) using a chlorine resistant cationic polymer (polyquaternary amine) of approximately 50000 of molecular weight. In both works a bench scale pilot filter having a 14 cm filter bed (mean grain diameter 0.6 mm) with porosity 0.4 and operated at 5 m/h was used. The experiments were performed at pH 5.5-6.

Stoichiometry between initial humic concentration and optimum polymer dose for both destabilization and filtration was observed. For example, the optimum polymer dose for the filtration of a 10 mg/l humic acid solution was twice that for a 5 mg/l solution and, in addition, the head loss across the filter bed at the termination of the filter run was twice as high for the 10 mg/l humic water. The authors concluded that filtration and coagulation are analogous processes as the optimum polymer dose for filtration was the same as the optimum dose for destabilization in the jar test, and the polymer doses which produced over and under-dosing in the jar test also produced similar effect in the filtration. It was noted however that colour was more efficiently removed in the filtration tests than in the jar tests, probably because in the direct filtration the formation of a settleable floc is not important.

Yet in these studies, Edzwald showed that the provision of a flocculation period prior filtration resulted in a significant decrease in head loss development. This inverse relation between particle size (for a given mass of particles) and head loss development was previously observed by Habibian and O'Melia (1975) for other colloidal system. It was also observed that the increase of the molecular weight of the polymer only had a beneficial effect on the removal efficiency when some flocculation period was provided.

Similar findings concerning filtration performance, the analogy between coagulation and filtration, and stoichiometry are reported by Edzwald (1979) in a pilot study employing dual media direct filtration for the removal of colour. As expected, head loss development was less than for single media filters, and longer filter runs were achieved.

More recently, Edzwald at al. (1982, 1987) discussed the effects of raw water quality, pH, coagulant type and dosage as well as some physical filtration variables (filtration rate, flocculation period and temperature) on the performance of the direct filtration. Such a discussion is based on the results of an experimental work with a large scale pilot dual media filter and two natural coloured waters. Both waters were low in turbidity but with considerably different concentrations of organic matter, mean TOC values of 4.0 and 7.5 mg/l. In each case alum and three cationic polyelectrolytes (polyquaternary amine) were used as coagulants. Filtration performance was evaluated by using both traditional parameters - head loss, filtered water turbidity and colour - and TOC and THM precursors removals.

The three polymers were effective in treating both waters by direct filtration. Whereas optimum polymer dosages varied from one polymer to another, the actual positive charge added was very similar for all polymers and agreed well with the estimated amount of negative charge associated with the organic matter in the raw water. It was observed that while the demand of polymer for effective filtration was not affected by the variation in the turbidity (1.2 to 6.5 NTU) of the raw water over the time of the experiments, it was significantly affected by changes in the concentration of organic matter (2.7 to 15 mg/l TOC). It is suggested that polymer requirement for coagulation is controlled by the concentration of the dissolved organic matter rather than by the concentration of particulate.

A comparison of the results for 'in-line' direct filtration against direct filtration preceded by flocculation showed that, although the effect on removal was not significant, the length of the filter run can be increased by providing a flocculation period, as a result of a decrease in the head loss development. The reduction in head loss may be due to a better distribution of the deposit across the filter bed as a result of applying to the filter the fewer and larger floc particles formed during flocculation. It is interesting to note that this phenomenon was not observed for the water with the lowest turbidity and TOC, in this case it is thought that number of floc particles generated by coagulation is so small that the flocculation kinetics is very low and aggregation does not occurs within a reasonable time. Filtration rate and water temperature did not have a significant effect on removals. Lowering the pH to 5.5-6.4, however, produced slightly better removals than treatment at pH 6.7-7.5.

Based on the results of these and previous works the authors suggested that the use of direct filtration using cationic polymers as sole coagulant is limited to raw waters with low to moderate TOC values, less than 5 mg/l, which is roughly equivalent to waters with 70 to 80 Hazen units of colour. For waters with higher TOC levels the polymer doses would be to high and costly, and the quality of the treated water would not be satisfactory in terms of TOC and THM precursors.

For each water, higher removals of TOC and THM precursors were obtained with alum than with any of the three polymers. The authors however do not recommend the use of alum in direct filtration of waters with high TOC concentrations since very high doses of alum would be required and, even under well-controlled pH, precipitation of aluminium hydroxide could occur leading to short filter runs. In those circumstances the use of alum/cationic polymer combination or even conventional treatment might be considered.

Rebhun et al. (1984) investigated the effect of filter bed grain size and polymer dose on contact flocculation-filtration of humic substances using alum as sole coagulant and alum plus a cationic polyelectrolyte as filtration aid. When alum was used alone with a medium grain (0.62 mm) sand at 5 m/h removal was good but an early breakthrough occurred. With the addition of polymer filtration quality improved and no breakthrough was observed, but filtration was terminated due to rapid head loss buildup.

With a coarse filter media (1.21 mm) alum alone showed an inefficient clarification. The co-addition of polymer at an optimum dose led to good clarification, moderate head loss development and acceptable filtration run time, although this time was observed to be shorter than that for filtration of mineral dispersions. Thus, contact flocculation-filtration of humic dispersions with alum at the optimum dose would be most efficient when a coarse media filter and a cationic polymer filtration aid at a well selected dose are used; lower and higher doses than the optimum give shorter filtration runs.

Using the experimental results Rebhun and co-workers calculated the following filtration parameters:

- Filtration removal coefficient (λ) in Iwasaki and Ives equations;
- Attachment and detachment coefficients in Adin and Rebhun equations;
- Head loss deposit relationship - Shektman's formula;
- Theoretical filter capacity and density of accumulated deposit.

The calculation showed that the solid content and the density of the alumo-organic deposits were much lower than of alumo-mineral deposits. The co-addition of polymer was shown to increase both solid content and density of the accumulated deposit, as well as increase the mass filter capacity. It was observed that the maximum λ was achieved when the optimum polymer dose was used in conjunction with alum. The values of the attachment and detachment coefficients calculated indicated that in the contact flocculation-filtration of humic substances initial filtration (attachment) is rapid and efficient, but the resistance to detachment or to disturbance forces is low. The low filtration capacity and the high detachment coefficient are consistent with the early breakthrough (cf. mineral suspension) observed experimentally.

The use of direct filtration preceded by alum coagulation at low pH values to remove humic substances has been investigated by Fettig et al. (1988). Although colour removal up to 90 percent were obtained on preliminary jar tests (0.45 µm membrane filtration) at an optimum pH between 5.5-5.9, floc separation in that pH range, by both direct filtration or sedimentation, was not efficient. Floc filterability was shown to be good at pH 4.75 but deteriorated dramatically between pH 5 and 6, improving again at pH>6. The changes in floc filterability were attributed by the authors to changes in the chemical structure of the floc. Because at low pH (<5) the ultimate removal of colour is not enough to achieve acceptable levels of colour of the filtrate, the authors suggest that the technical application of low-pH direct filtration must also involve stabilization of water followed by a second filtration (pH>6). In this way, the benefits of the excellent filterability of the alum-humic floc for pH<5, and probably high filter capacity, could be used for the removal of most of the organic material present in the water and only a small amount left has to be removed in the subsequent filtration.

1.4 Objectives of the study

The discovery that humic substances act as precursors in the formation of trihalomethanes (THM) during the chlorination process (Rook, 1974), and that the THM may be harmful to the human health, have focused attention on the needs of improving the removal of colour (humic substances) from drinking waters.

Since in the pH of most natural waters the humic substances are dissolved (stable) negatively charged polymers, the removal of colour from water bodies involves, in most water treatment schemes, a preliminary step of destabilization/coagulation. From the investigations described in section 1.2, it can be seen that colour can be successfully destabilized by both hydrolysing coagulants and cationic polyelectrolytes.

Due to the characteristic low turbidity of most coloured waters, they are regarded as natural candidates to be treated by direct filtration. Thus, coagulant-assisted direct filtration is a common method for treating upland, coloured surface waters in Scotland and Northern England.

A significant number of those water treatment works in England and Scotland that use direct filtration for the treatment of coloured waters regularly use aluminium sulphate as coagulant. However, operational problems related to the use of alum have often been reported (Cookson, 1987; Britton and Cochrane, 1989; Gregory, personal communication), particularly during the periodical increase of colour concentration in the raw water. Such problems include: (i) difficulties in maintaining economic filtration runs because of the high alum demand - the formation of considerable amounts of flocculated material lead to unacceptable short filtration runs; (ii) failure to meet the requirements of the European Community Drinking Water Directive (CEC, 1980) for residual aluminium and colour.

To overcome the above problems partial or complete replacement of alum by cationic polymer has been suggested. As shown in sections 1.2 and 1.3, although some investigations are reported on the use of cationic polymer as sole coagulant or as filtration aid, very little has been done about the partial replacement of alum.

Taking into account this scenario the present study was conceived and set out to achieve two broad aims:

(i) to evaluate the effect of partial replacement of alum by a cationic polymer on the performance of direct filtration of coloured waters, and investigate how cationic polymers act in conjunction with aluminium in precipitating organic colour;

(ii) to investigate the characteristics of the flocs formed when alum is used in combination with cationic polymer to coagulate coloured waters, and how such characteristics correlate with the filtration performance.

To accomplish these objectives the investigation was divided into three parts, each of them corresponding to a section in this dissertation. These sections are summarized below.

Section 2: describes the field work undertaken in order to extract, from a naturally coloured water source, the humic substances necessary to carry out the investigation. The extraction method used was reverse osmosis followed by freeze drying. Since the extracted material was to be used in the preparation of the synthetic coloured water employed in the filtration experiments, a characterization study of both extract and synthetic water was also undertaken. The results obtained are presented and discussed.

Section 3: describes the laboratory-based experiments designed to evaluate the effect of using different alum-cationic polymer combinations on the treatability of coloured waters by direct filtration. The variation of the filtration performance with the use of different coagulant combinations was studied using a matrix approach. For that, filtration tests were carried out at different pre-treatment conditions varying from coagulation with alum-only to coagulation with polymer-only, passing through various alum-polymer combinations via systematic reduction of alum dose. For each experiment, the filtration performance was estimated using Ives' Filterability Number. Stoichiometric effects were evaluated by performing the filtration tests with two different colour concentrations.

Section 4: describes the experimental work related to the characterization of the flocs formed under the various pre-treatment conditions tested in the filtration experiments. The floc characteristics studied were floc size (volume) distribution and floc charge.

The results obtained in section 3 and 4 are discussed in section 5, and a summary of the main observations and conclusions are presented in section 6.

2. EXTRACTION AND CHARACTERIZATION OF THE HUMIC MATERIAL

2.1 Introduction

Extraction and/or isolation of humic substances from their natural environment (soil, sediments and water) is usually a time consuming and laborious process. In the aquatic environment this task is particularly difficult due to the low concentration of humic substances in natural waters as compared to concentrations in soil and sediments. As a result, very large volumes of water must be processed to obtain a few grams of humic material. In addition, the purchase of, and familiarity with, specialized equipment and procedures are usually necessary in order to isolate humic substances.

For these reasons some researchers, in the various areas of investigation related to humic substances, opt for the use of commercially available humic substances, commonly called humic acids. In the water treatment literature these commercial humic substances, as well as specially prepared humic extracts, are used to prepare synthetic coloured waters by dissolving the humic extract in distilled or tap water (Hall and Packham, 1965; Mangravite et al.,1975; Narkis and Rebhun, 1975, 1977; Glaser and Edzwald, 1979; Scheuch and Edzwald, 1981; Edwards and Amirtharajah, 1985; Dempsey at al., 1984, 1985 and various others). The advantages of using such synthetic waters are: (1) samples of a standard water can be easily created on demand; (2) the humic substances used to produce it are, in a number of cases, already characterized.

The use of commercial humic matter as representative material for natural humic substances has been examined by Malcolm and MacCarthy (1986). By analyzing the nuclear magnetic resonance (NMR) spectra, the infra-red (IR) spectra and the elemental composition of various commercially available humic material, and comparing them with similar measurements of representative humic substances extracted from soil and water, they found that the commercial products are distinctly different from soil and water humic substances and therefore are not representative of soil and water humic and fulvic acids. Moreover, the commercial materials are quite similar among themselves regardless of the manufacturer suggesting that these materials probably originate from a common type of source. Malcolm and MacCarthy also point out the lack of information about origin and method of extraction used in the production of such humic materials.

Amy et al. (1985) when contrasting the results of the coagulation of natural and synthetic waters prepared from soil extracted humic matter, including some commercial products, reported: "The use of soil extracted humic substances in water treatment research has potential merit if caution is exercised in the interpretation and applicability of the results. Based on this research, soil extracted humic acids do not accurately simulate the behaviour of aquatic humic substances.....It appears that soil-extracted fulvic acids have some merit in approximating the behaviour of aquatic humic substances".

Differences in behaviour between humic substances from soil and water are explained by their different compositions. In the aquatic environment the fulvic acid fraction predominates by a factor 9:1 over the humic acid fraction (Malcolm, 1985), while in soil the humic acid fraction is in very large excess over fulvic acid. Moreover, the molecular structure of aquatic humic and fulvic acid differ from their soil counterparts. Whereas the typical average molecular weight values are 800-1000 daltons for aquatic fulvic acid and 2000-3000 daltons for aquatic humic acid, for soil humic acid molecular weights are reported to be as large as several hundred thousand daltons (Suffet and MacCarthy, 1989).

In the present work, taking into account the above considerations, it was decided to extract the humic substances from a natural coloured water source instead of using any commercial humic material.

Numerous methods to concentrate and/or isolate humic substances from water are available in the literature, some of them are: freeze-drying, chemical co-precipitation, ultrafiltration and reverse osmosis. There are also a number of sorption methods on different sorbents such as alumina, carbon, ion exchange resins and nonionic macroporous resins. The methods commonly used are summarized by Thurman (1985) and Aiken (1985), among others. In his work Aiken (1985) points out that by employing a variety of methods the isolation of aquatic humic substances can be more efficient and yield to a high quality product. Table 2.1 presents the advantages and disadvantages of some of these methods.

In recent years, adsorption on nonionic macroporous resins has been a very popular method among American researchers to extract and fractionate humic matter, and its use is recommended in the extraction procedure outlined by the International Humic Substances Society (IHSS). In the general procedure the water is acidified to pH<2 and passed through a column containing the resin (e.g. cross-linked polymethyl methacrylate, XAD-8). The humic substances sorb into the hydrophobic resin while the more hydrophilic non-humic materials pass through. To remove the fulvic and humic acid fractions from the resin it is eluted with sodium hydroxide at different pH conditions. The two fractions are then converted to their hydrogen form by passage through a strong cation exchanger in the hydrogen form.

Although the use of macroporous resins is generally considered a good method of isolation and fractionation of humic substances, the use of sodium hydroxide as eluent in this process is considered one of its main disadvantages. During desorption precautions are required to prevent oxidation of the humic substances.

Connor (1986), when comparing infra-red spectra of alkali and non-alkali extracts from natural coloured waters, noticed an increase in both the level of oxidation and the degree of unsaturation in the alkali extracted material suggesting chemical changes, possibly, of irreversible character in the humic composition. He pointed out that previous studies by other researchers indicate that strongly alkaline pHs, particularly in the presence of air, cause oxidation of humics, usually accompanied by irreversible darkening, an effect also observed by Connor with his alkali extracts.

Method	Advantages	Disadvantages
Vacuum distillation	1. Low temperatures.	1. All solutes concentrated.
Freeze-drying (Lyophilization)	1. Mild. 2. High concentration factors. 3. Sample taken to dryness.	1. Method is slow. 2. All solutes with the exception of volatiles are concentrated.
Freeze concentration	1. Mild. 2. Inexpensive. 3. Simple.	1. Method is slow. 2. All solutes concentrated.
Coprecipitation	1. Inexpensive. 2. Effective for waters high in DOC.	1. Efficiency dependent on initial DOC. 2. Inefficient on large volumes of water. 3. Isolated organic matter must be separated from inorganic salts.
Ultrafiltration	1. Organic solutes fractionated by molecular size. 2. Large volumes can be processed.	1. Interactions with membrane possible. 2. Fouling of membrane possible.
Reverse osmosis	1. Ambient conditions, mild. 2. Large volumes can be processed.	1. All solutes concentrated. 2. Efficiency dependent on concentration.
Solvent extraction	1. Inorganic salts effectively excluded.	1. Humic substances insoluble in many solvents. 2. Method is slow.
Sorption		
Alumina	1. Organic acids readily sorb to basic adsorbent. 2. Mild eluents.	1. Inefficient desorption. 2. Structural alterations of organic matter possible.
Nylon and polyamide powder	1. Efficient adsorption.	1. Irreversible sorption probable.
Carbon	1. Inexpensive. 2. Simple procedure. 3. Large volumes of water can be readily processed. 4. Organic blanks are low.	1. Irreversible sorption possible. 2. Slow elution rates. 3. Slow sorption rates with high-molecular-weight species. 4. Chemical alteration of organic solutes possible.
Anion exchange (a) Strong-base resins	1. Method is simple. 2. Large volumes can be processed. 3. High capacities for macroporous resins.	1. Irreversible sorption probable. 2. Fouling of resins possible. 3. Resin bleed. 4. All anions concentrated.
(b) Weak-base resins on amphoteric matrix	1. Method is simple. 2. Large volumes can be processed. 3. High capacities for macroporous resins. 4. Efficient desorption. 5. Inorganic salts removed.	1. All organic anions concentrated. Humic substances must be isolated from hydrophilic acids. 2. Extensive cleanup of resin required. 3. Resin bleed. 4. Desorption with NaOH.
Nonionic macroporous sorbents	1. Method is simple. 2. Resins easily regenerated. 3. Large volumes can be processed. 4. High capacities. 5. Efficient desorption of acrylic ester resins.	1. Irreversible sorption possible on styrene divinylbenzene resins. 2. Desorption with NaOH. Precautions required to prevent oxidation of humic substances. 3. Resin bleed. 4. pH adjustment to pH 2 prior to adsorption.

Table 2.1: Methods commonly used to isolate and concentrate aquatic humic substances (after Aiken, 1985)

The above observations, and the fact that in the present investigation the volume of water to be processed in order to produce the necessary amount of humic material to carry out the experiments was evaluated to be about 10000 litres, did not favour the use of macroporous resins. A preliminary calculation showed that the volume of the column (resin volume) needed to process, in a reasonable time, such volume of water would be enormous. In addition, the infrastructure necessary to run the column would probably not be available on the site where the actual extraction would take place.

An option to deal with very large volumes of water is the use of reverse osmosis. Reverse Osmosis (RO) is the opposite phenomenon of natural osmosis. In natural osmosis, when two solutions of different concentrations are separated by a semi-permeable membrane the solvent flows spontaneously from the diluted to the concentrated solution - the membrane impedes the passage of the solute but allows solvent flow. As a result, the level of the concentrated solution rises until the pressure set up by the liquid column counterbalances the flow (osmotic pressure), establishing the so called osmotic equilibrium. In reverse osmosis the solvent is forced through the membrane from the concentrated to the diluted solution and, in this way, concentration takes place. It occurs when a pressure greater than the osmotic pressure is exerted on a solution in contact with a semi-permeable (selective) membrane.

As a method of concentrating organic matter from water, reverse osmosis has the advantage of operating under ambient conditions, therefore minimizing the possibility of destructive chemical reactions (Deinzer et al., 1975, Aiken, 1985). Furthermore, high values of retention of organic material in the 'concentrate' can be achieved (Kopfler et al., 1975; Odegaard and Koottatep, 1982; Aiken, 1985). The disadvantage usually attributed to RO is the fact that other non-humic solutes, both organic and inorganic, are also concentrated leading to a non-purified concentrate. In this work however, the presence of other water constituents than just humic substances was welcomed since it was believed that a coloured solution prepared from a non-purified extracted material would have a composition closer to that of natural coloured waters. In other words, the aim was to have an extracted material which would produce a synthetic coloured water with similar characteristics to natural coloured waters but with a desired colour intensity.

In order to assess the practicability of using a commercially available reverse osmosis equipment to perform the task of concentrate the humic substances, contact with a commercial supplier was established and a suitable type of equipment and membrane were identified.

To evaluate the degree of concentration of humic substances attainable with this equipment, water samples from two potential extraction sites were tested by the supplier. Theoretical calculations and operating data suggested that one of the water samples could be concentrated 13 times and the other 18 times. It was believed however, that in view of the fact that the membrane was going to be used on a 'one off' basis, higher concentrations would be likely.

Using the conservative figure of 18 times concentration, the original volume of 10000 litres of water could be concentrated to 550 litres. This reduced volume of water containing a high concentration of organic matter would then need to be further treated by another method. So, bearing in mind the initial commitment of avoiding any chemical-involving processes, freeze drying was chosen as the secondary method.

Freeze drying is considered a gentle method of concentration of humic substances from water (Malcolm, 1968), high concentration factors are possible with the advantage that the sample can be taken to dryness. The solid product obtained can be easily handled and stored without fear of chemical degradation which is the reason why freeze drying is commonly used in combination with other concentration methods as a final step in extraction procedures (IHSS; Thurman and Malcolm, 1981; Liao and Randtke, 1985).

2.2 Extraction of humic material - Experimental

The equipment used was a tubular reverse osmosis mobile unit (Paterson and Candy International, England) operated in batch and in the recycle mode as shown in figure 2.1.

The unit was fitted with a 12 feet long membrane module with a membrane area of 2.7 m^2. This module is basically a stainless steel cylinder (permeate collection shroud) containing 18 small diameter stainless steel perforated 'support' tubes connected in series. Each support tube holds a paper tube where the membrane film is cast inside. This design, according to the manufacturer, allows operation at uniform high solution flow velocities to minimise fouling of the membrane. The membrane used was a non-cellulosic type membrane (ZF99, Paterson and Candy International) of size cut-off 100, that can be operated at relatively high temperatures (up to 60°C at 60 bar) and over a wide pH range (3 to 11 up to 60°C).

The reverse osmosis unit was installed at the raw water inlet chamber at Eccup Water Treatment Works - Yorkshire Water. During the period of extraction two different raw waters were concentrated. Initially the raw water came from a group of reservoirs (Washburn Water) and had an apparent colour in the range of 70-85 Hazen units and low turbidity (table 2.2). A raw water volume of about 7 m^3 was concentrated to 600-700 litres and, subsequently, reconcentrated to a final volume of 120 litres.

	pH	App. Colour (Abs/m)	Turbidity (FTU)	Conductivity (µS/cm)
Mean value	6.9	5.0	4.0	150
Std. deviation	0.1	0.3	0.6	24
Maximum value	7.1	5.2	4.8	175
Minimum value	6.8	4.6	3.3	127

Table 2.2: Washburn water characteristics during concentration period

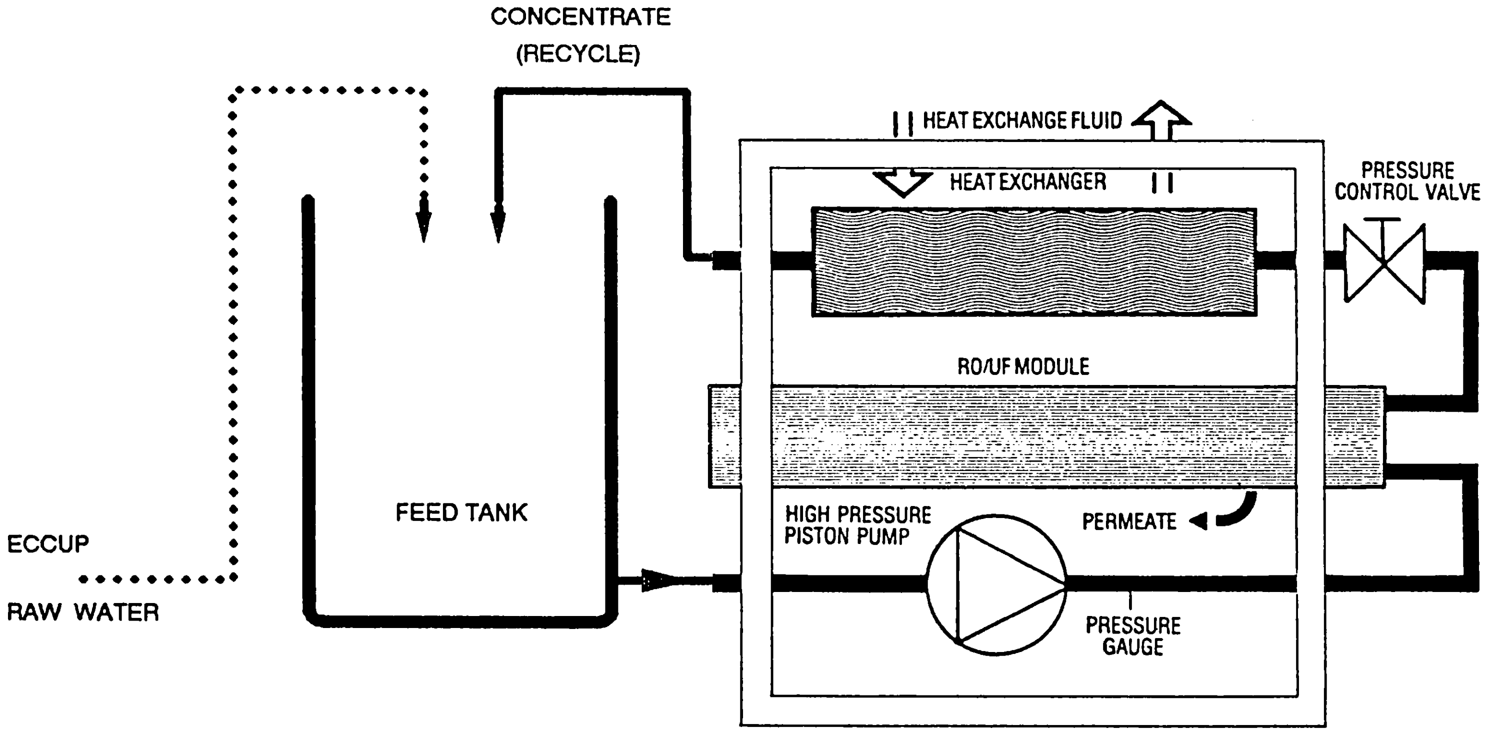


Figure 2.1: Humic substances concentration - Reverse osmosis unit schematic diagram

Due to operational problems Yorkshire Water had to start using water from an additional source, the River Ouse, changing the nature of the raw water going to Eccup WTW. This blended water (Washburn-Ouse) had a lower colour concentration and a significantly higher turbidity. An additional 6 m^3 of the blended water was concentrated and reconcentrated leading to a final volume of 100 litres.

Absorbance measurements (colour concentration) carried out for the two concentrated waters are presented in table 2.3. They show the effect of the raw water characteristics on the degree of colour concentration.

	Absorbance Units/metre *	
	Washburn	Washburn-Ouse
Raw water	2.6	-
1st concentration	28.7	25.1
2nd concentration	94.3	54.6

* Measured at 380 nm after filtration through 0.45 µm membrane

Table 2.3: Colour intensity during the concentration process

The concentrated samples were freeze dried by Commercial Freeze Drying, Clitheroe, England. The samples, initially frozen at -18°C, were dried over four days under a pressure of 0.3 mB and with a shelf temperature (heating temperature) of 15°C. The resulting dried material amounted to 650 grams from Washburn concentrate and 1050 grams from Washburn-Ouse concentrate.

It should be noted that the two samples were handled and kept separated during the whole process of concentration and freeze drying.

2.3 Reconstituting the coloured water

The coloured water used in the laboratory experiments was prepared by dissolving in high purity water (Milli-Q, Millipore, Harrow) the necessary amount of dried material to obtain the desired colour intensity. The dissolution of the dried humic material was aided by placing the solution in an ultrasonic bath for 1-2 minutes. Tests carried out elsewhere (Whittle, 1988) for the same humic materials indicated that the ultrasonic treatment did not affect the molecular weight distribution of the humic material. The undissolved material was subsequently removed by passing the solution through a glass microfibre filter (Whatman GF/C, Whatman International Ltd., Maidstone, England) of pore opening 1.2 microns, by this means the reconstituted coloured water had virtually no turbidity.

Reconstituted water with two colour intensities were required to perform the filtration experiments - one to be representative of a source with moderate colour, and the other to be representative of a fairly high coloured water. In order to determine the amount of dried material necessary to prepare these synthetic waters a series of solutions with different concentrations of extract were prepared and had their colour compared with platinum-cobalt standards by means of a comparator disc unit (Lovibond Nessleriser).

2.4 Characterization of the reconstituted water

To validate the use of the reconstituted coloured water as a 'model' of natural coloured waters, characteristics of the reconstituted water were determined and compared with data from the literature. In addition, some degree of characterization of the humic substances present in the dried extracted materials was also undertaken.

2.4.1 Material and methods

The main techniques used in the characterization of the reconstituted water were ultra-violet visible spectroscopy and organic carbon analysis. Other parameters, like alkalinity, conductivity, solid content etc, were also measured. For the characterization of the humic substances themselves, infra-red spectroscopy and gel permeation chromatography were used.

The methodologies and equipment used in the characterisation work are briefly described below.

Ultra-Violet Visible Spectroscopy

The UV-visible absorbance spectra were determined using a scanning spectrophotometer Pye Unican SP8-100 (Pye Unican Ltd., Cambridge) supplied with chart recorder. A pair of 40 mm quartz cells were used. The normal scanning procedure was followed and it is described in the manufacturer's manual.

Fixed wavelength measurements were also performed in the same equipment always using 40 mm quartz cells, unless otherwise stated.

Total Organic Carbon - TOC

The TOC concentrations were measured using a Dohrmann DC-80 Total Organic Carbon Analyzer (Envirotec Dohrmann, USA).

The equipment utilizes the ultraviolet promoted persulphate oxidation technique. The oxidation product, CO_2, is analyzed in a non-dispersive infra-red (NDIR) detector which is sensitive to CO_2. The NDIR produces an electrical output (peak) which is integrated and scaled by the number processor and the result is displayed as milligrams of carbon per litre (mg C/l).

Unfortunately, the DC-80 is not able to differentiate carbon dioxide generated from the oxidation of inorganic and organic compounds present in the sample, and therefore the value obtained by this analysis is in fact the amount of total carbon (TC), where the total carbon = total organic carbon (TOC) + total inorganic carbon.

Alkalinity and solid content were measured following the procedure described in the "Analysis of Raw Water and Waste Water" (Department of Environment, 1972). Conductivity was measured directly by using a pH/conductivity meter.

Infra-Red Spectroscopy

The infra-red spectra of aquatic humic substances are usually similar and there are a number of common adsorption frequencies. Because of their similarity they can be used as a comparative procedure in the characterization of humic substances. An infra-red spectrum by itself can give only limited information about the functional groups present.

The IR spectroscopic measurements for both extracts were carried out by the Water Research Centre (WRc, Stevenage). The dried extracts were prepared for the infra-red analysis as 1% (w/w) potassium bromide discs. The equipment and method used are described elsewhere (Connor, 1986a).

Gel Permeation Chromatography - GPC

Gel permeation chromatography was used in this investigation in an attempt to determine the molecular weight distribution of the humic substances present in the extracts.

The gel permeation chromatography apparatus consisted basically of a chromatographic column connected to an on-line differential UV-detector, at a wavelength of 254 nm, linked to a trace recorder. A schematic diagram is shown in figure 2.2.

The gel permeation materials used in this study were Bio-gel P-100 and P-10 porous polyacrylamide beads (Biorad, USA) suitable for

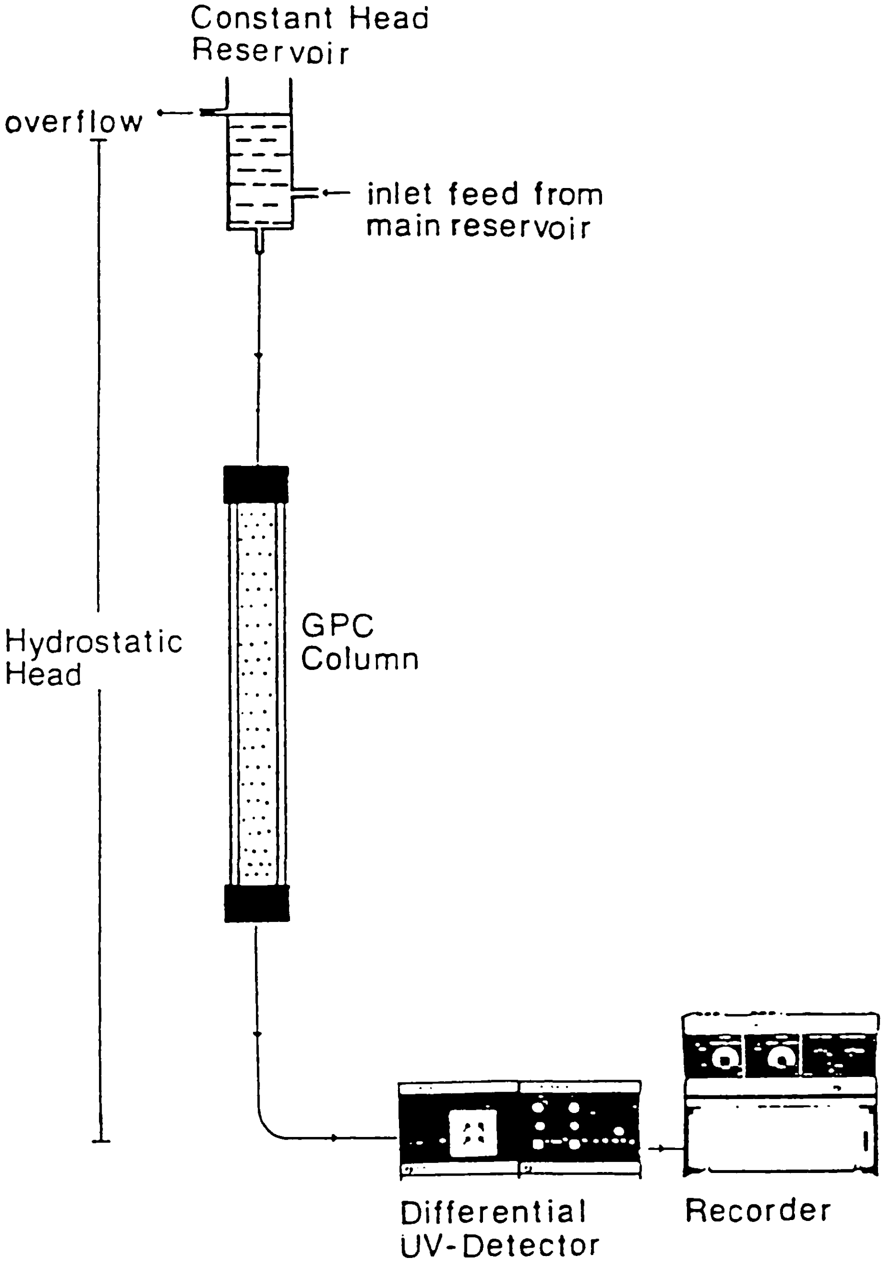


Figure 2.2: Schematic diagram of the apparatus for Gel Permeation Chromatography (after Whittle, 1988)

high resolution gel filtration. Some properties of these materials are listed in table 2.4.

Gel type	Wet Mesh Designation	Diameter of Hydrated beads (micron)	Fractionation range (dalton)	Hydrated Bed Volume ml/g dry gel
BG P-100	100-200	80-150	5000-100000	15
BG P-10	100-200	80-150	1500-20000	9

Table 2.4: Technical information for Bio-gel P-100 and P-10 (after Whittle, 1988)

The Bio-gel P columns were calibrated with appropriate proteins of known molecular weight (MW). The calibration curves are shown in figure 2.3 and the operation conditions are described in table 2.5.

Gel type	Bed Weight (cm)	Hydrostatic Head (cm)	Column Flow (cm^3/h)
Bio-gel P-100	45	90	4-6
Bio-gel P-10	45	40	15-20

Table 2.5: Operating conditions for Bio-gel P (after Whittle, 1988)

For the determination of the molecular weight distribution of the humic extracts, the elution volume for the peak resulting from a humic sample run was calculated from the column flow rate and trace distance and the MW range determined from the appropriate calibration curve. The eluent used was 5% v/v Tris Buffer, considered optimal to minimise potential interactions. Both eluent and humic solution had the pH adjusted to 9 prior to testing.

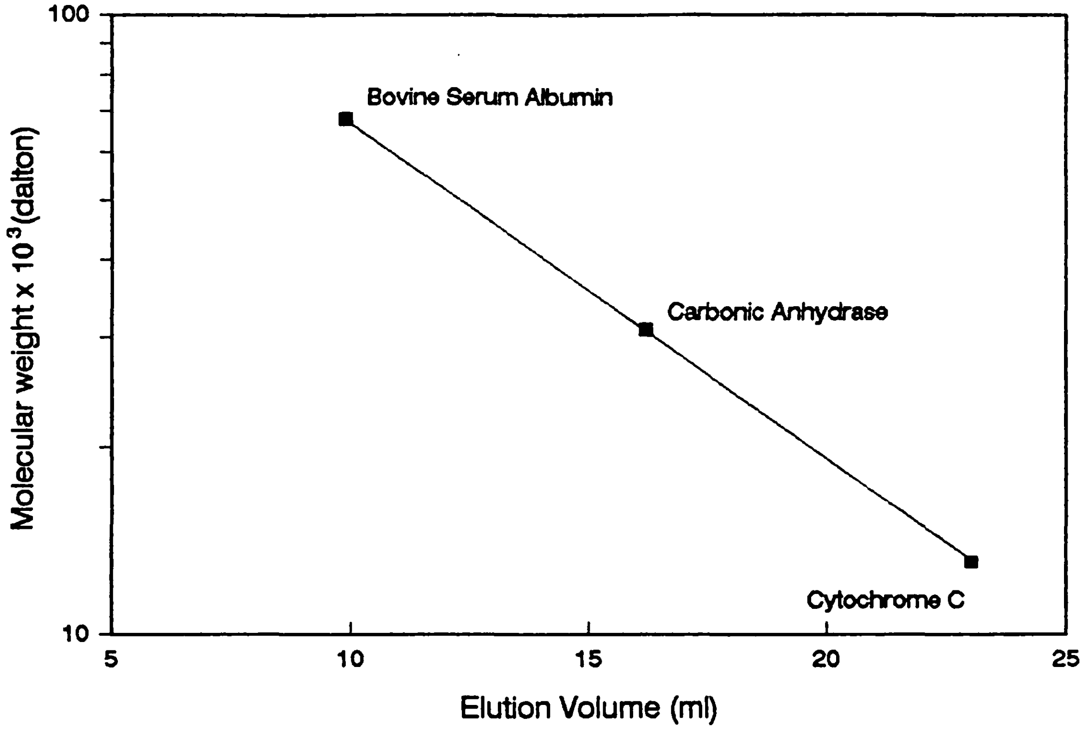


Figure 2.3 a: Calibration curve for Bio-gel P-100

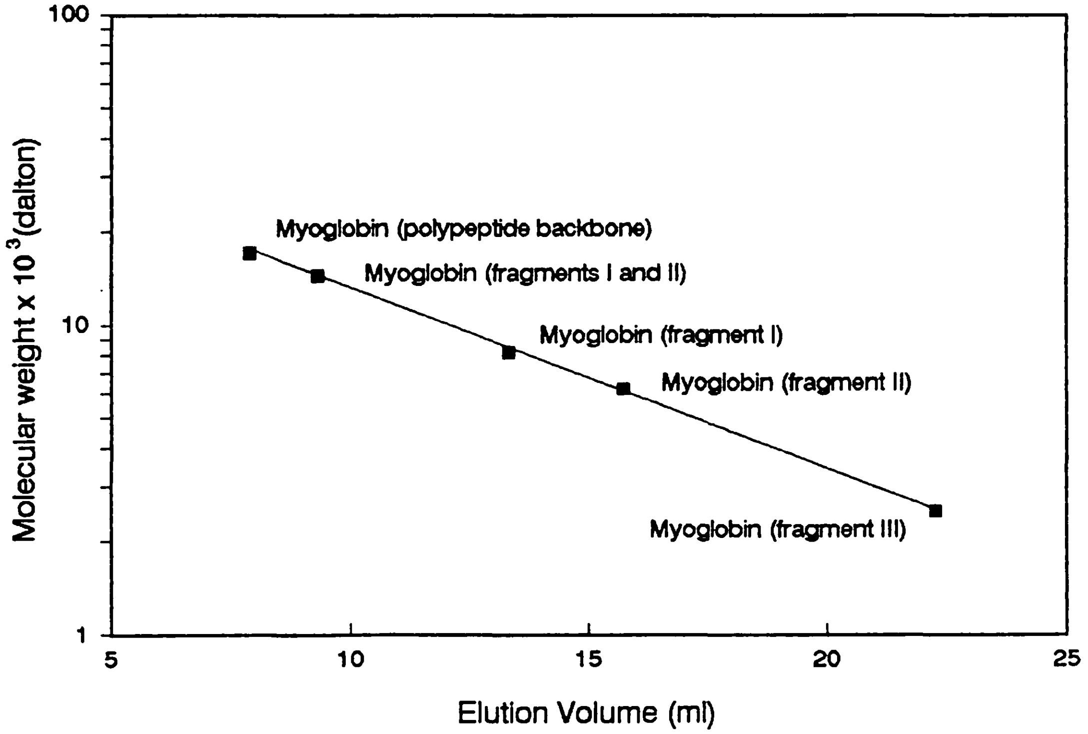


Figure 2.3 b: Calibration curve for Bio-gel P-10

A detailed description of the method, apparatus, calibration and measurement procedures is reported by Whittle (1988).

2.4.2 Results and discussion

Although the characterization work undertaken in this investigation has dealt with both, Washburn and Washburn-Ouse, humic extracts, particular attention is given to the results obtained for the Washburn extract, since this extract was the one selected to perform the filtration experiments.

The first step in the direction to validate the use of the reconstituted water as a representative model of a natural coloured water was the determination of the UV-visible absorbance spectra.

The spectra of various solutions made up with different concentrations of both dried extracts were determined within the range from 200 to 800 nm using the procedure described previously. A typical result obtained for each reconstituted water is shown in figure 2.4.

The spectra obtained (figure 2.4) follow the characteristic pattern observed by many researchers for various natural coloured waters and humic substance solutions (Black and Christman, 1963; Stevenson, 1971; Thurman, 1985; Connor, 1986, 1986a and others). The spectra are featureless with no absorption band and the absorption increases with the decreasing wavelength. The fact that the spectra are featureless indicate a complex structure which causes overlapping of absorbance bands.

This lack of any characteristic absorption bands may be the reason for the diversity of wavelength values being used to measure colour and/or humic substances in aquatic systems. To illustrate this fact a number of values reported in the literature are presented in table 2.6.

In this investigation it was chosen to use wavelength 400 nm basically because around this wavelength absorbance measurements of coloured waters and of Pt-Co standard solutions present similar values.

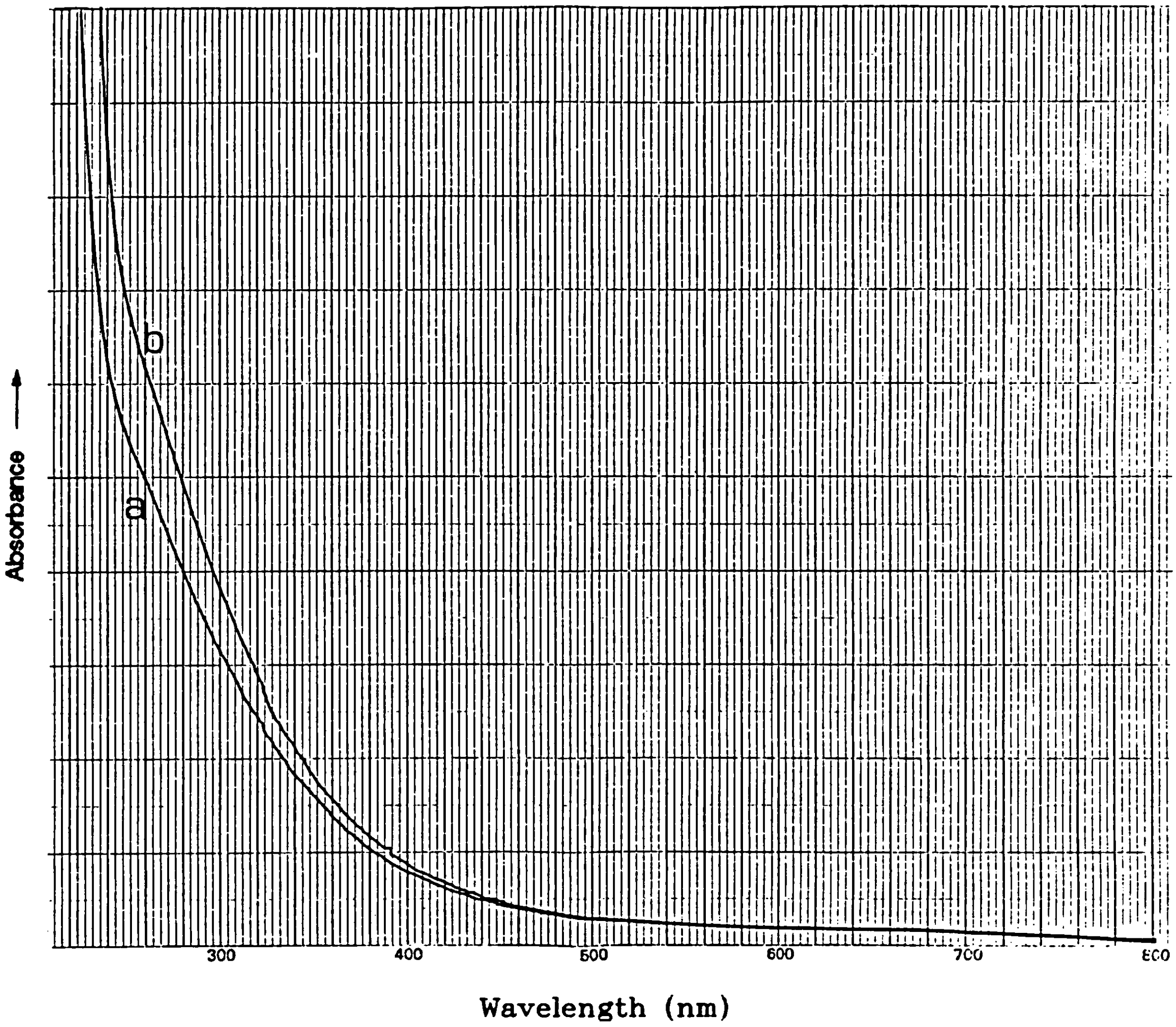


Figure 2.4: UV-Visible absorbance spectra of humic solutions
(a) Washburn extract (b) Washburn-Ouse extract

Wavelength (nm)	References
254	Dempsey et al., 1984, 1985; Vik et al., 1985
260	Semmens and Field, 1980
310	Amy and Chadik, 1983; Chadik and Amy, 1983
385-470	Department of Environment, 1972
400	Packham, 1973; Jackson et al., 1988
412	Crowther and Evans, 1981
420	Edzwald and co-workers,
422.2	Edwards and Amirtharajah, 1985
430	Babcock and Singer, 1979
550	Mangravite et al., 1975

Table 2.6: Wavelengths used to measure humic substances in water.

Crowther and Evans (1981) showed, by measuring the absorbance spectra for humic solutions and Pt-Co Standards which impart the same colour intensity, that they only absorb the same amount of light at two points where the two spectra cross, 412 and 460 nm. At the lower wavelength the response of the equipment is higher.

The use of a measurement that can be easily correlated to Pt-Co (Hazen) units has the advantage of making possible the comparison of the data from this work with a large number of practical data from water treatment plants. Also, in England and Wales the Water Authorities have been using absorbance at 400 nm to represent the amount of colour in natural and treated waters.

As can be seen from figure 2.5 the concentration of dried extract is linearly related to absorbance measurements at 400 nm and therefore follows Beer's Law. When the reconstituted water solutions are individually prepared a slight deviation from Beer's Law is observed at high concentrations of extract due to dissolution problems. It was noted that the amount of undissolved residue remaining from high concentration solutions was comparatively higher than the amount remaining from the lower concentrations, indicating that the concentration of dried extract affects the efficiency of dissolution. However, for samples obtained by diluting a concentrated stock solution no deviation from Beer's Law is observed which supports the theory that the deviation is associated with the dissolution of the extract.

In the last few years there has been a trend to use 254 nm wavelength to measure dissolved humic concentration. It is considered that at this wavelength absorbance measurements are more representative of the total organic matter (Edzwald et al., 1985). To evaluate the effect of using this wavelength, absorbance values obtained at 254 nm for various solutions with different concentrations of Washburn humic extract were compared with those obtained at 400 nm. The result is shown in figure 2.6. As expected, the values are linearly related with a very high correlation coefficient, suggesting that both wavelengths can be used to express the amount of humic substances (colour) in water.

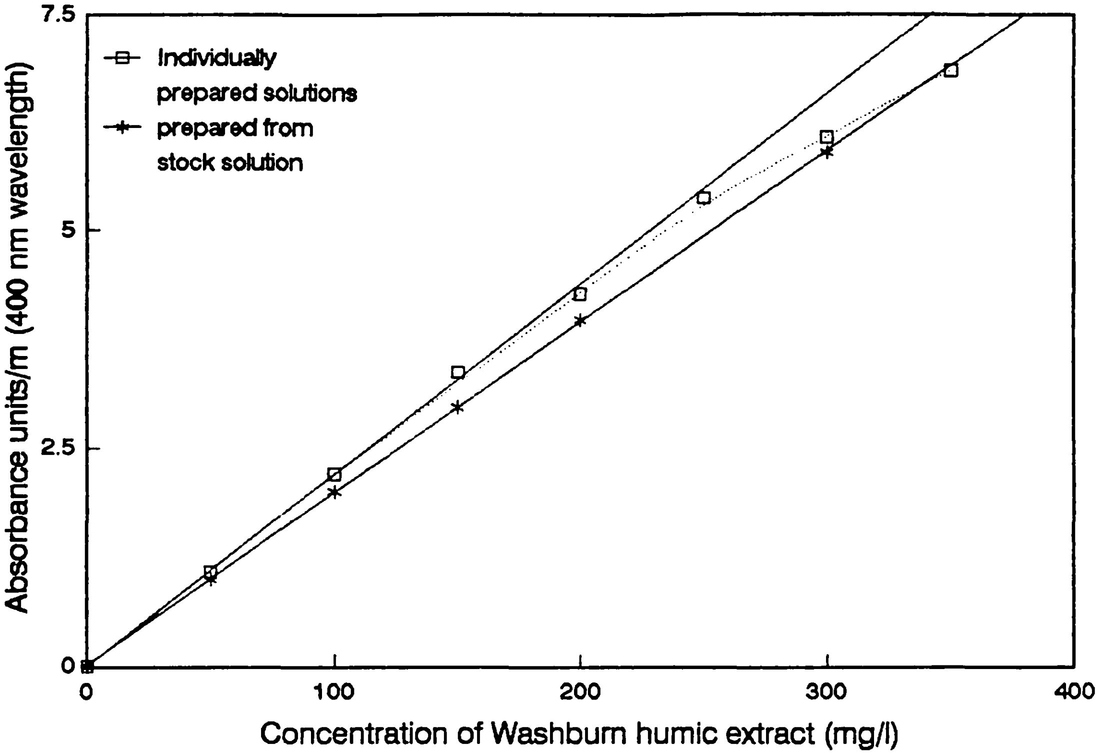


Figure 2.5: Beer's Law verification

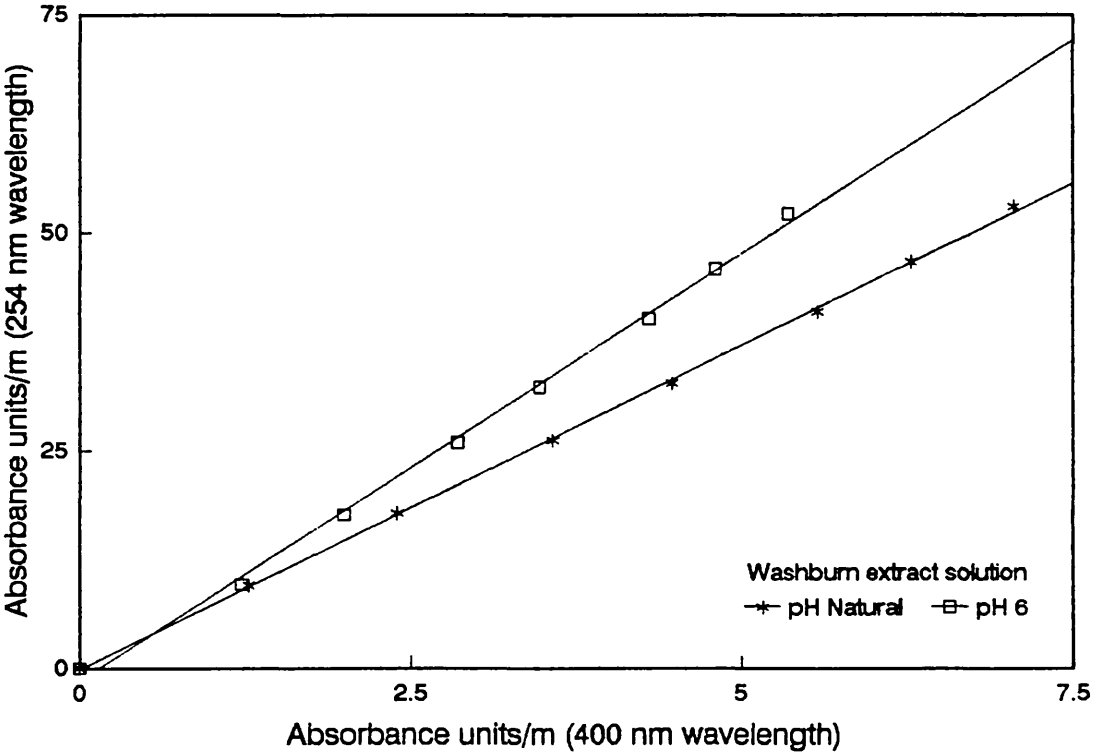


Figure 2.6: UV - Visible measurements correlation

The relation between colour, as Hazen units, and absorbance of reconstituted water samples (Washburn extract) measured at 400 and 254 nm wavelength were also evaluated and the results are presented in figure 2.7. At 400 nm the two parameters are related by the equation ***Colour = 18.1 x Abs/m - 4.4*** and the value of the slope is close to the average conversion value used by the Water Authorities in England, where 1 Abs. unit per metre at 400 nm is equal to 14 Hazen units of colour (Mantle, 1989). The slope of the curve obtained at 254 nm wavelength is, although in the same range, lower than those reported by Vik et al. (1985) for various Norwegian lake waters. A strict comparison of values is hindered by the fact that both absorbance and colour are affected by changes in pH.

The various concentrations of reconstituted water samples were also analyzed in terms of total carbon-TC. The results obtained were then related to the absorbance measurements previously done and can be seen in figure 2.8. The TC/absorbance ratio values obtained in this study were observed to be 15 to 50% higher than the values reported by other researchers for a number of coloured natural waters and humic substance solutions (Edzwald et al., 1985; Vik et al., 1985). Besides the differences inherent to each particular water source, it is important to consider in this comparison the fact that parameter measurements were performed, in each case, at different conditions. In the present investigation, due to the limitation of the equipment used, the total carbon (organic + inorganic) was measured whereas in the other studies considered the parameter analyzed was the total organic carbon. Moreover, the absorbance measurements were not carried out at the same pH value in all studies. It has been shown previously (Hall and Packham, 1965; Singley et al., 1966 and others) that the intensity of organic colour in water increases with the increase of pH. This was confirmed in this investigation as presented in figure 2.9.

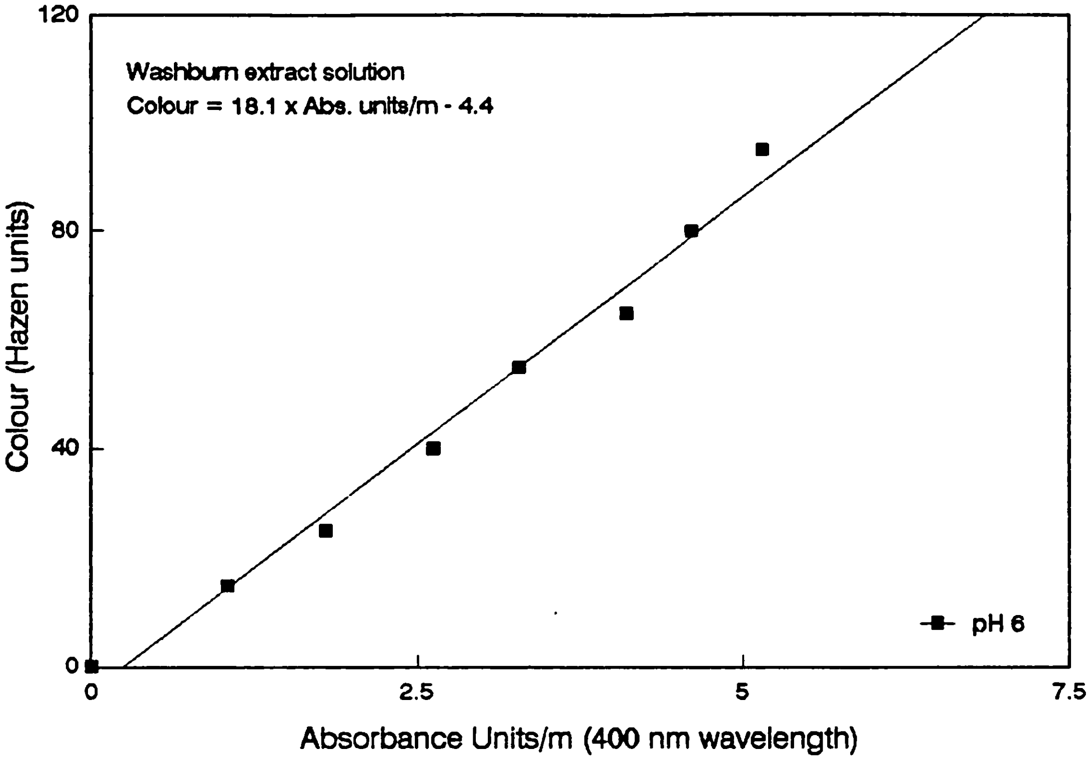


Figure 2.7 a: Colour - Absorbance (400 nm) correlation

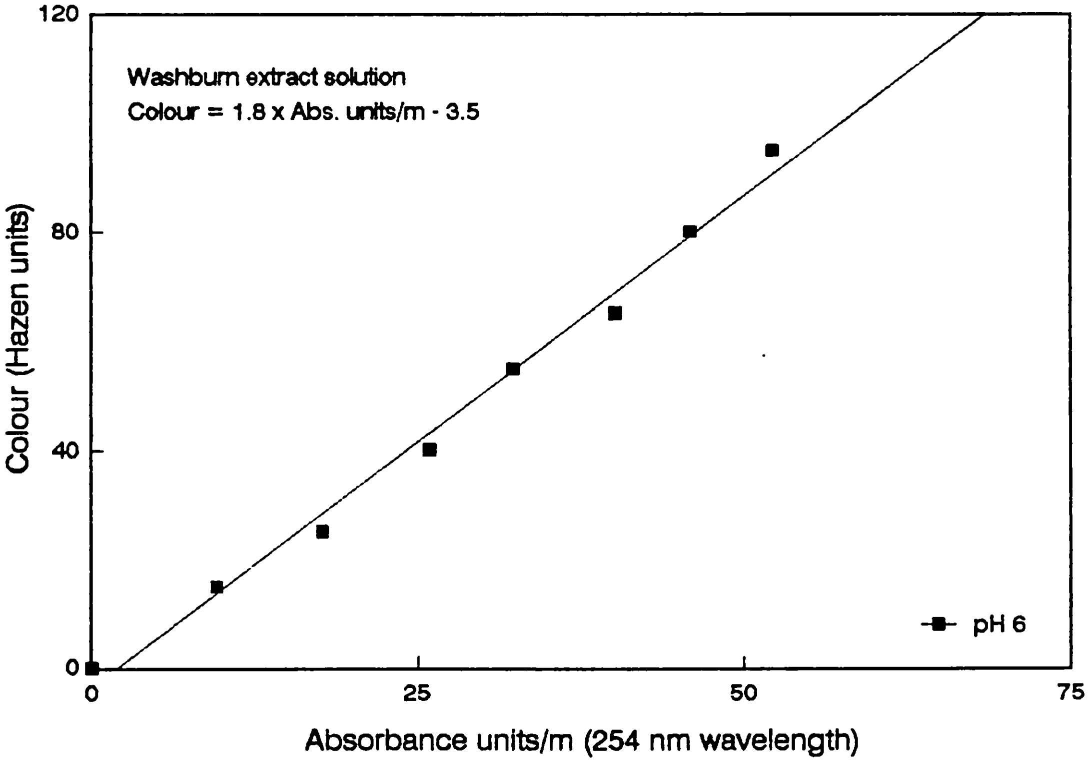


Figure 2.7 b: Colour - Absorbance (254 nm) correlation

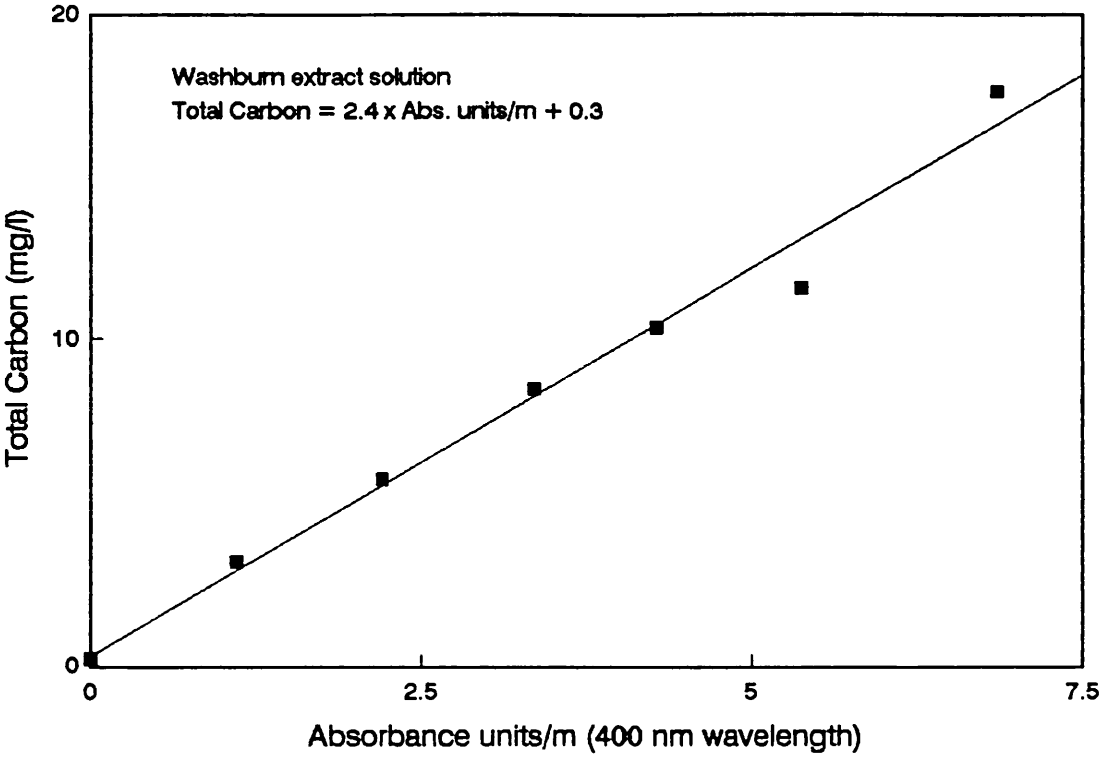


Figure 2.8 a: Total Carbon - Absorbance (400 nm) correlation

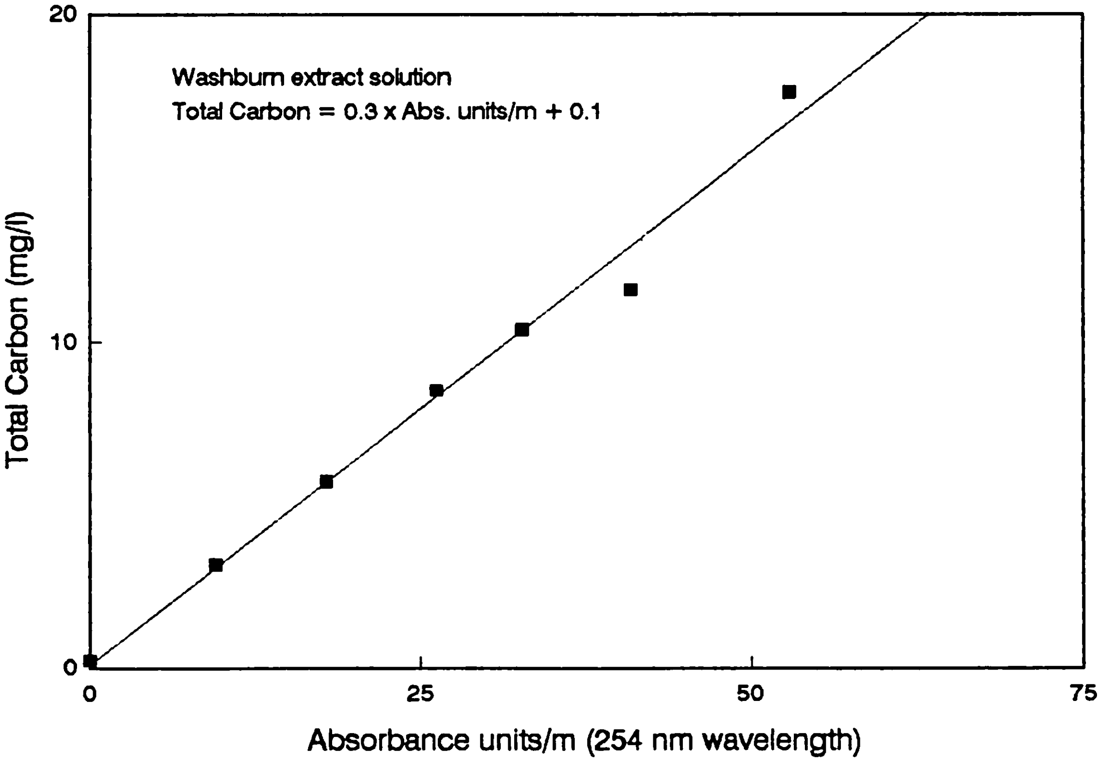


Figure 2.8 b: Total Carbon - Absorbance (254 nm) correlation

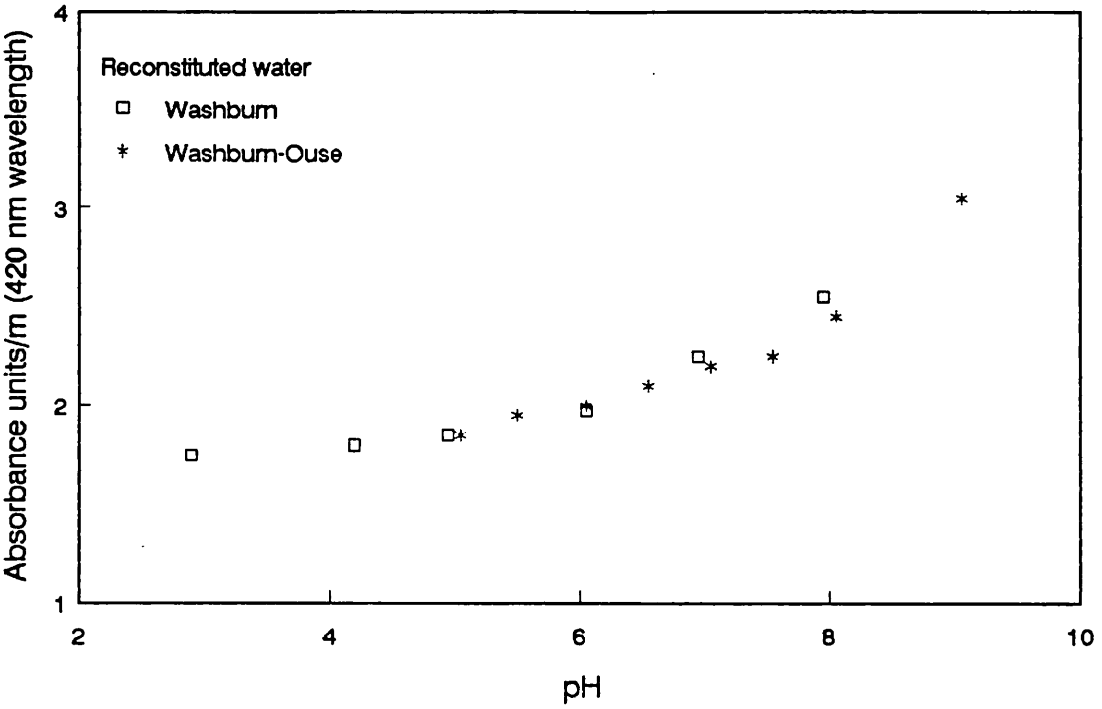


Figure 2.9: Colour variation with pH

Based on colour comparison the concentrations of extracted material to make up the reconstituted water to be used during the experimental work were chosen. Concentrations of 150 mg/l and 300 mg/l of extracted material from Washburn source were adopted as representative of a moderate and high coloured waters, respectively. Some physical and chemical parameters were measured for both Washburn solutions and for a 500 mg/l Washburn-Ouse solution. The results are shown in table 2.7.

An inspection on the values of total alkalinity, TOC and conductivity presented in table 2.7 shows that these parameters are in the characteristic range of a moderate to high coloured soft upland water. However, it can be seen that the pH of the reconstituted water is considerably higher, probably due to the loss of dissolved gases, mainly CO_2, during the extraction process. The values of turbidity for the reconstituted waters are made deliberately low by filtering the solution through a microfibre filter of 1.2 µm pore opening.

	Washburn		Washburn-Ouse
	150 mg/l	300 mg/l	500 mg/l
Total Solids (mg/l)	140	-	442
Total Volatile Solids (mg/l)	53	-	282
Total fixed solids (mg/l)	87	-	160
Total dissolved solids (mg/l)	128	-	372
Total suspended solids (mg/l)	13	-	71
Total Carbon* (mg/l)	10.7	19.7	17.6-20.3
pH	9 to 9.5	9 to 10	≈9
Total alkalinity* (mg/l $CaCO_3$)	14	22.5	55
Conductivity* (µS/cm at 25°C)	180	-	501
Colour* (Abs. units/m$^+$)	2.55	4.9	3.05
Colour* (Hazen units) pH 6	40	80	-
Turbidity* (NTU)	0.3	0.4	-

* filtered through 1.2 µm microfibre filter $^+$ measured at 420 nm

Table 2.7: Characteristics of extracted humic material solutions

The above evidences suggest that the reconstituted water prepared with the extracted materials from Washburn and Washburn-Ouse water can be used as a reasonable representative model for coloured waters.

The infra-red spectra determined for Washburn and Washburn-Ouse extracts are shown in figure 2.10. Both spectra are very similar to each other and to those spectra presented by Connor (1986a) for a number of humic extracts from coloured water from Northern England and Scotland.

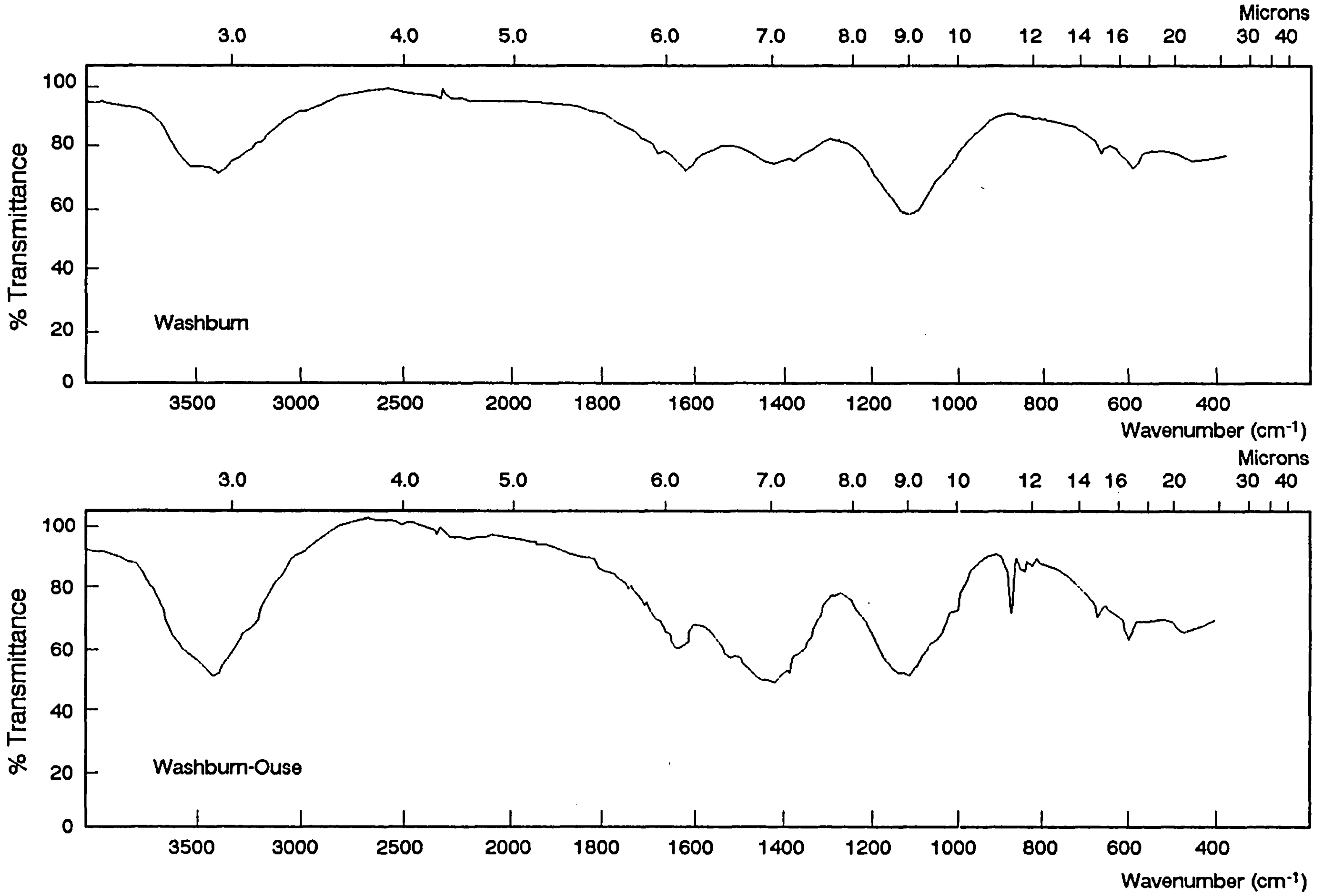


Figure 2.10: Infra-red absorbance spectra for Washburn and Washburn-Ouse humic extracts

The main adsorption bands in both Washburn and Washburn-Ouse extracts occur at 3400 cm^{-1}, 1630 cm^{-1}, 1450-1410 cm^{-1} and 1110 cm^{-1}. The lack of a sharp absorbance peak near 1720 cm^{-1} (C=O stretch of carboxylic acids), commonly reported as the characteristic adsorption band of fulvic acids (Stevenson, 1971; Thurman, 1985), is probably due the fact that the extracts were not purified prior to analysis and the humic substances present were in their salt forms. In the salt form, the carbonyl peak is shifted to lower wavenumbers because of electron donation of the carboxylic group. This is supported by presence of strong carbonyl peak near 1630 cm^{-1} and 1400 cm^{-1} (stretch of C=O in carboxylate - Thurman, 1985). Similar behaviour were observed for Connor's extracts spectra (Connor, 1986a)

The molecular weight distribution measurements for the Washburn and Washburn-Ouse humic extracts were carried out by R. Whittle (Whittle, 1988), a postgraduate student in the Department of Civil Engineering, Imperial College, as part of the requirements for the degree of Master of Science.

Preliminary determinations of molecular weight were done by using the Washburn-Ouse material and Bio-gel P-100. The Washburn-Ouse extract was chosen to test the outlined procedure by convenience, since there was no restriction about material availability. The results obtained are summarized in table 2.8.

Humic Solution Concentration (g/l)	Elution Volume (ml)	Molecular Weight Range (dalton)
0.5	32.5 - 29.2	< 5000*
6.0	18.6 - 42.1	13300 - < 5000*

* Below the resolution of the column

Table 2.8: Effect of the concentration of humic extract on molecular weight distribution (Bio-gel P-100) (after Whittle, 1988)

As can be seen, the concentration of the extract solution has a strong effect on the molecular weight distribution, with a broad MW range being detected at the higher concentration. The results also suggest that the low end of the distribution consists of molecules with less than 5,000 daltons and therefore, out of the range of the Bio-gel P-100 column.

Based on these results a decision was made to use the Bio-gel P-10 in order to obtain more accurate results. Table 2.9 shows the results obtained for the two humic extracts.

Humic Solution Concentration (g/l)	Elution Volume (ml)	Molecular Weight Range (dalton)
0.5 Washburn	3.7 - 6.9	≥ 20000*
1.0 Washburn-Ouse	10.2 - 14.4	12400 - 7150

* Above the resolution of the column

Table 2.9: Molecular weight range of humic substances extracts (Bio-gel P-10) (after Whittle, 1988)

It is quite difficult to analyze the results showed in table 2.9, since the MW of Washburn extract is outside the resolution of the column. However, these results indicate that the two extracts have a very distinct molecular weights distribution ranges.

According to Whittle (1988) the difference in MW distribution is probably due to differences in the chemical nature of the humic species present in the Washburn-River Ouse blended water and those present in the Washburn water since humic substances in rivers and reservoirs are originated from different precursors. However, the fact that the major contribution for the blended Washburn-Ouse water was from the Washburn source does not support the above hypothesis. On the contrary, it suggests that both extracts should have, at least, a common range of molecular weights.

It was shown previously (table 2.8) that the concentration of the extract solution has a strong effect on the MW distribution. Since a solution containing 0.5 g/l of Washburn extract is known to be considerably more concentrated in humic substances than a 1 g/l solution of Washburn-Ouse extract some differences in MW were expected. However, this fact alone does not explain the magnitude of the difference obtained.

Another unexpected feature in the results is the lack of low molecular weight products in any of the extracts, contradicting the results initially obtained with the Washburn-Ouse extract (table 2.8). In a recent publication (Thurman, 1985) a summary of MW determination results from various works is presented and shows that the molecular weight of the majority of aquatic humic substances are less than 10000 with a significant percentage of them being less than 5000.

Again, the non-purified character of the extracts may account for some interference in the measurements by imparting an apparent high molecular weight resulting from molecule-impurity-molecule interaction. However, it seems unlikely that the extent of these interactions were enough to mask completely the low molecular range.

In summary, it is considered that the above measurements do not provide sufficiently reliable evidence to allow conclusions about the molecular weight of the humic substances under consideration to be made.

2.5 Conclusions

1. Reverse osmosis followed by freeze drying is an efficient method of concentrating humic substances from natural waters and they are able to deal with high volumes of water in a relatively short time.

2. The reconstituted waters from Washburn and Washburn-Ouse extracts were shown to be similar in behaviour to other natural coloured waters.

3. Characterization of the humic substances present in reverse osmosis/freeze dried extracts are compromised by the non-purified nature of the material. If characterization is to be pursued, purification and fractionation is suggested before freeze drying the sample.

FILTRATION EXPERIMENTS

3.1 Introduction

The removal of colour from drinking water assumed a new importance in the mid 70s with the discovery that the chlorination of natural waters can lead to the formation of haloforms and that the humic substances acts as haloform precursors (Rook, 1974).

Due to the characteristic low turbidity of most coloured waters direct filtration has been suggested as an attractive alternative to treat such waters. In spite of this potential suitability, direct filtration of coloured waters has not been extensively investigated and few studies have been reported in the literature up to the present time.

The use of different coagulants and their effect on the ability of direct filtration of removing colour/total organic matter from natural waters was investigated by Edzwald and co-workers (Edzwald et al., 1982, 1987). They concluded that direct filtration using alum or cationic polymers as sole coagulant is limited to low to moderate coloured water (TOC less than 5 mg/l). However, the use of an alum-polymer combination is suggested as an option to treat highly coloured waters. Rebhun et al. (1984) showed that the use of cationic polymers in combination with alum can improve direct filtration (contact filtration) of humic substances as a result of an increase of the density of the accumulated deposit in the filter bed.

The effect of different alum-cationic polymer combinations on the treatability of coloured waters by direct filtration is evaluated in the present study using a matrix approach. For that, filtration tests were performed at different pre-treatment conditions varying from coagulation with alum only, to coagulation with polymer only, passing through various alum-polymer combinations via systematic reduction of alum doses. The filtration experiments were carried out at a constant pH and the filtration performance comparatively evaluated by means of a filterability index.

Preliminary coagulation tests were done in order to select the pH value to be used in the filtration experiments as well as to establish the range of coagulant doses of both alum and polymer to be studied.

Two coloured water intensities prepared from Washburn extract were used for both jar and filtration experiments, allowing the evaluation of stoichiometric effects.

3.2 Experimental

3.2.1 Coagulation test

The coagulation experiments were carried out using a six place multi-speed mixing unit 'jar test' apparatus (Aztec Environmental Control Ltd., Oxon). The procedure used allowed the coagulation tests to be performed at specific pH values.

Essentially, the procedure consisted of pH adjustment followed by coagulant addition and rapid mixing plus a final slow mixing period. The initial pH adjustment was carried out by adding to the raw water samples (250 ml of water in 500 ml beakers) an appropriate amount of hydrochloric acid (HCl) or sodium hydroxide ($NaOH$) so that after addition of the coagulant the desired pH value of the mixed solution is achieved. The necessary amount of acid or base to be added was calculated using combined titration curves where coagulant dose and the volume of acid or base are plotted against the pH of the mixed solution. The coagulant (alum or polymer) was then added to the water samples and mixed vigorously (200 rpm) over 3 minutes. During this time the pH of each jar was monitored and a fine adjustment was carried out if necessary. The solutions were then gently mixed (30 rpm) for a further 17 minutes.

In order to evaluate the efficiency of the coagulation-flocculation process the coagulated water samples were filtered through a Whatman GF/C microfibre glass filter and the residual colour, and in some cases residual aluminium, were measured following the procedure described below (section 3.2.3).

3.2.2 Filtration test

3.2.2.1 Filtration apparatus

The bench scale experimental filtration apparatus, shown in plate 1, comprised a feeding system, mixing device, coiled tube flocculator and filter bed column.

A schematic diagram of the apparatus is presented in figure 3.1.

Feeding system and mixing device

The mixing device, an 'H' shaped flow connector drilled in a perspex block (plate 2), was designed to promote an instantaneous rapid mixing of the three flows entering the flocculator.

The coloured water and the alum solution are initially mixed in a 'T' configuration branch with directly opposed flow paths (see figure 3.2). Less than a second later, they are mixed with the polymer solution which is injected immediately prior to a 90° sharp elbow. The calculated velocity gradient for the alum-raw water mixing was about 1500 s^{-1} and for the addition of polymer the value was approximately 1400 s^{-1}. The sudden expansion of diameter from the mixing device to the flocculator promotes an additional mixing of the three flows. The chemical addition sequence was based on previous work (Bowie and Bond, 1977 and Edzwald et al., 1977).

The three flows were delivered from the feed tanks to the mixing device by means of two variable speed peristaltic pumps (Watson-Marlow 502S, Watson-Marlow Ltd., Falmouth). A double head pump was used to feed the coloured water and aluminium sulphate solution, and a single head one was used for the polymer solution. By choosing the appropriate tube diameter and rotation speed, the flow rate of the pumps were set to the desired values. Rotameters (Planton Flow Bits, Basingstoke) were installed downstream of the pumps to monitor the flow rates.

Plate 1. The Set-up of Filtration Experiments

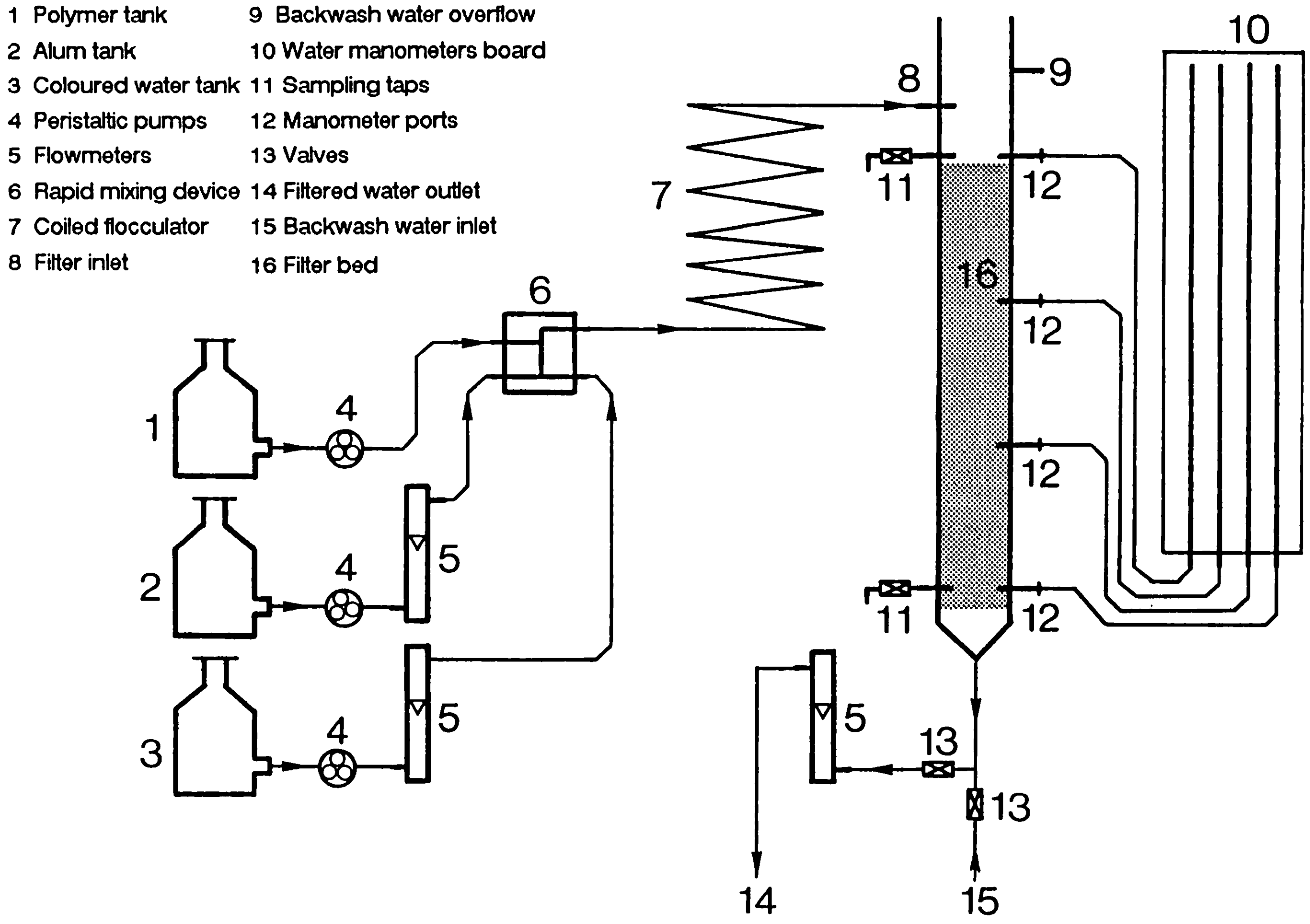


Figure 3.1: Schematic filtration apparatus

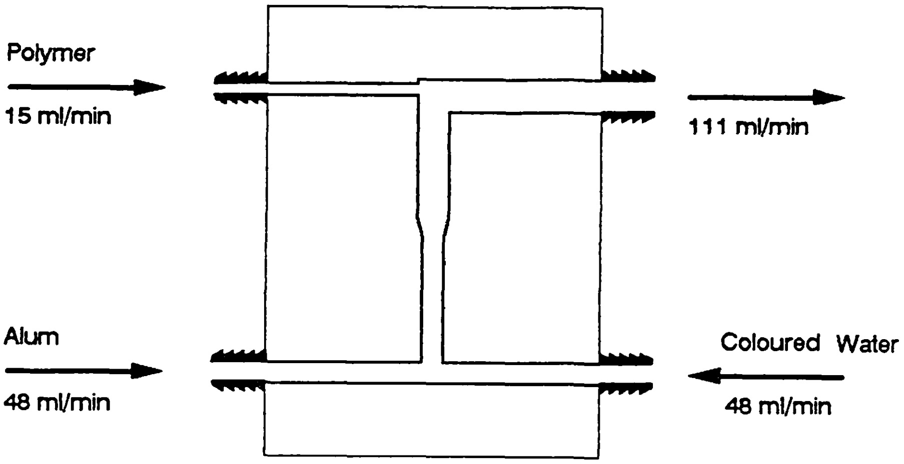


Figure 3.2: Flow mixing device

The mixing effectiveness was evaluated by means of a tracing test. Distilled water and a high concentration salt solution of known conductivity were pumped through the mixing device and the conductivity of the discharged flow was measured by a conductivity meter (PTl-20, Water Analyzer, Data Scientific). Mixing tests with contrasting coloured solutions were also carried out to allow visual inspection of the mixing pattern. Both methods demonstrated that the three flow were completely mixed at the discharge point.

Flocculator

A laminar flow tube flocculator was used. This device is convenient for laboratory scale flocculation due to its simplicity in design and operation. No mechanical parts are involved and the flocculation time can be easily modified by increasing or shortening the tube length without affecting the velocity gradient, which, for a specific tube diameter, depends only on the flow rate. Therefore, both velocity gradient and residence time can be varied independently.

The flocculator (plate 2) was made of a 30 metre long, 8 mm internal diameter, silicon rubber tubing coiled around a 38 cm diameter former.

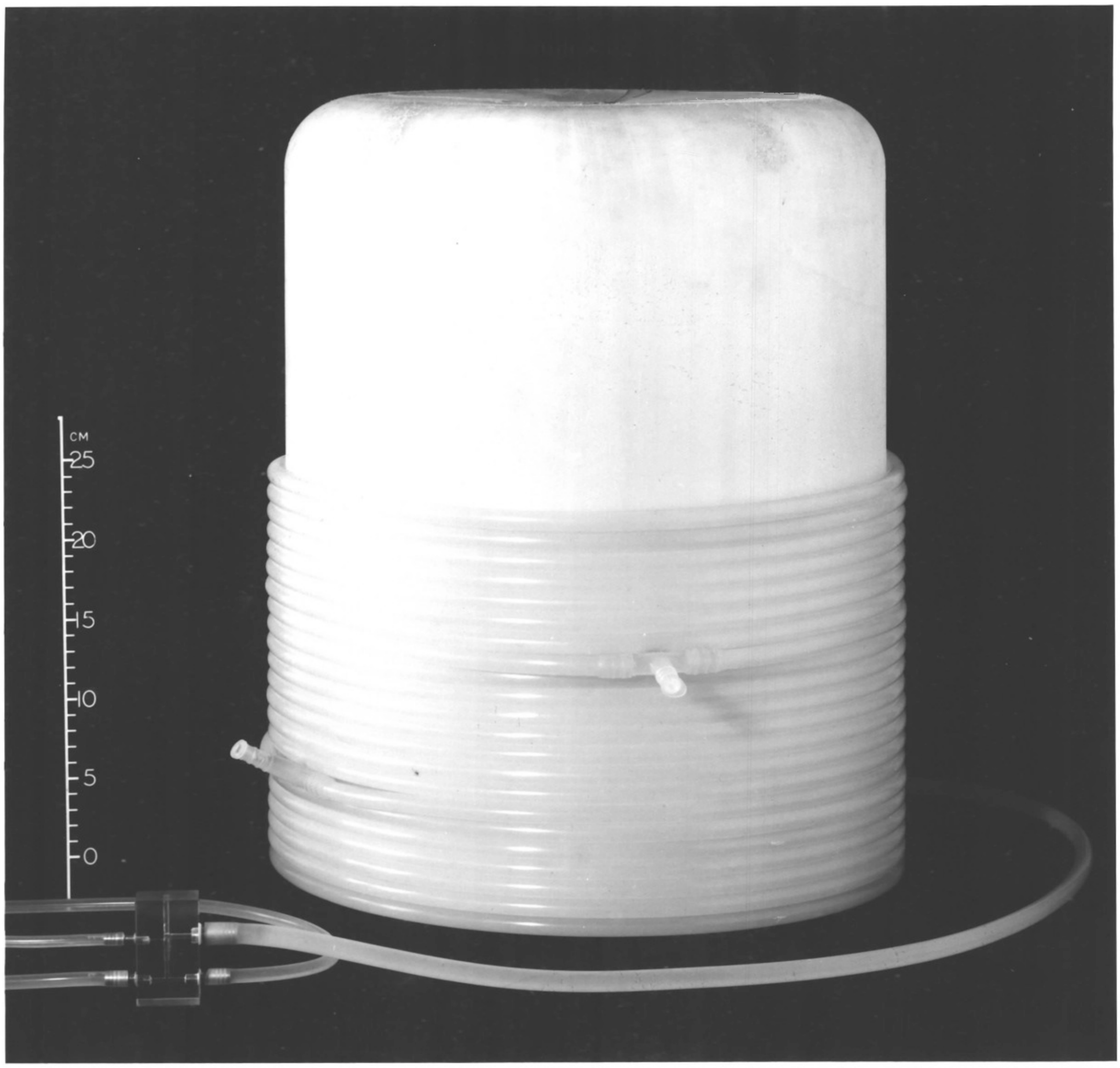


Plate 2. Mixing Device and Coiled Flocculator

The average velocity gradient (*G*) within the tube flocculator and the mean residence time (*t*) can be calculated by using equations (1) and (2) as follows (Gregory, 1981):

$$G = \frac{8Q}{3\pi R^3} \tag{1}$$

$$G\,t = \frac{8L}{3R} \tag{2}$$

Where Q is the volumetric flow rate

R is the tube radius

L is the total length of the tube

For the flow rate used in the filtration experiments (111 ml/minute) the theoretical values obtained for G and t were approximately 25 s^{-1} and 800 seconds (13.5 minutes) respectively, giving a Gt product of 20000. The actual G value occurring in the flocculator was determined by measuring the head loss across the length of the coiled tube. The relationship between the head loss and the velocity gradient in a laminar flow tube flocculator is given by equation (3) (Vigneswaran et al., 1984).

$$G = \sqrt{\frac{gQ\,\Delta H}{\nu\,V}} \tag{3}$$

Where V is the volume of the flocculator (ml)

ΔH is the head loss through the flocculator (cm)

g is the gravitational acceleration (cm/s^2)

ν is the kinematic viscosity (cm^2/s)

The actual *G* value turned out to be about 35 s^{-1} leading to a *Gt* of 28000, which is higher than the theoretical calculation, but still in the range of values used in practical flocculation units (Gregory, 1977, 1983).

Filter column

The filter column (plate 3) consisted of a 1000 mm length of 40 mm internal diameter glass tubing, containing a 500 mm filter bed. To support the bed and avoid losing filter medium a 30 mm layer of ballotini with diameter between 850-1000 microns was placed on 850 micron brass mesh located at the base of the column.

Water head within the column could be measured via four manometer ports positioned at 20 mm, 250 mm, 450 mm and 550 mm from the base of the column. The ports were connected via flexible PVC tubing to water manometer tubes mounted on a graduated board.

The feeding inlet, located 150 mm above the filter bed, was an 8 mm glass tube piece penetrating the filter column to 1/3 of its diameter and making a 90° angle with the filter wall. To minimize floc break up and attenuate the flow pulsing effect of the peristaltic pumps, the filter inlet was kept submersed during filtration.

The filtrate/backwashing arrangement consisted of a upside-down 'T' piece glass tube at the base of the column, provided with a valve in each arm to direct the flow. The filtrate water flow rate was controlled by a rotameter with a range of 20-280 ml/minute installed in the filtrate water line. The backwash flow rate was controlled by the backwash water feed pump and the overflow outlet was located 270 mm above the filter bed.

The filter medium (filter bed), whose characteristics are given in table 3.1, was composed of graded (600 to 700 microns) ballotini non-porous glass spheres (English Glass Co. Ltd., Leicester, UK) of nominal diameter 655 microns. Prior to use the ballotini was acid washed (10% HCl and 10% HNO_3 solution) to remove possible surface contamination.

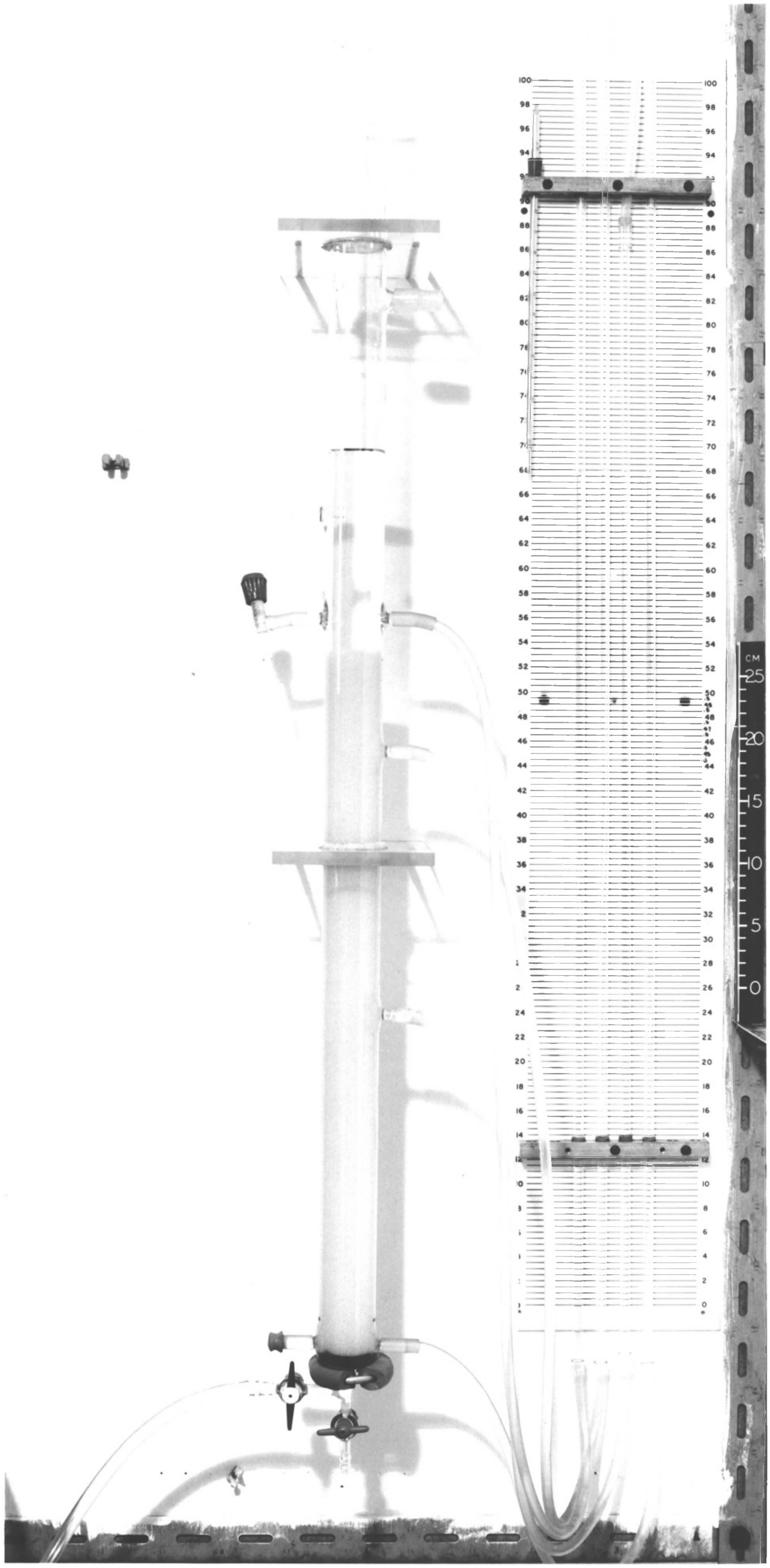


Plate 3. Filter Column

After a thorough rinsing with distilled water the ballotini was dried and stored until required.

Type	Ballotini glass spheres	
Composition	Lead glass	
	Principal constituents:	
	SiO_2	58%
	PbO	25%
	K_2O	9%
	Na_2O	4%
	B_2O_3	2%
Specific gravity	2.95	
B.S. sieve range	22 - 25	
Sphericity	spherical but percentage with irregular shapes not known	

Table 3.1: Characteristics of the granular filter media (after Graham, 1982)

The procedure described by Graham (1982) was adopted for laying of the filter bed. The empty glass column was initially filled with water and then progressively filled with ballotini to avoid air entrainment. In order to get the desired porosity value of 0.4, the appropriate weight of ballotini was packed to a previously determined column volume.

3.2.2.2 Experimental procedure

The experimental procedure can be divided in three stages: (1) the preparatory stage which include the solutions preparation and pH adjustment, (2) the filtration run itself and sample collection and (3) water quality analysis (described in the next section).

The reconstituted coloured water was prepared the day before the filtration run following the procedure described previously, whereas the polymer and aluminium sulphate solution were freshly prepared the day of the filtration test. The solutions were prepared taking into account the dilution occurred during the mixing process.

The pH adjustment, made immediately before the filtration run, was accomplished by the addition of a calculated volume of HCl or NaOH to the reconstituted coloured water so that the mixture leaving the mixing device achieved the desired pH value. Preliminary filtration tests showed that little or no change of pH occurs during the flocculation process.

Once the pH was corrected, the filtration run itself could be initiated. The filtration time counting was only started after 14 minutes, when the flocculated water reached the filter column. This time is the flocculation residence time, as calculated in section 3.2.2.1, and confirmed experimentally using a salt tracing solution. With this method the time necessary for a salt solution of known conductivity to replace the distilled water inside the coiled tube was monitored by measuring the conductivity at the discharge of the flocculator (curve **a** in figure 3.3).

Using the same method, salt conductivity tracing, the time needed for the flocculated water to displace the clean water above and within the filter bed and reach the outlet tubing was measured as 7 minutes. Hence, after 7 minutes of filtration time the accumulation of the filtered water in the treated water tank was started. The conductivity profiles of both flocculator and filter are shown in figure 3.3.

Two kinds of filtrate samples were collected for analysis during the filtration experiment: (i) 'instantaneous' samples taken directly from the filtrate outlet tubing every 10 minutes starting at 7 minutes, and (ii) 'composite' samples of the filtered water that was continuously accumulated in the treated water tank. In the latter, samples were taken from the tank at 60 and 90 minutes of filtration time and also at 120 minutes if the filtration run was that long.

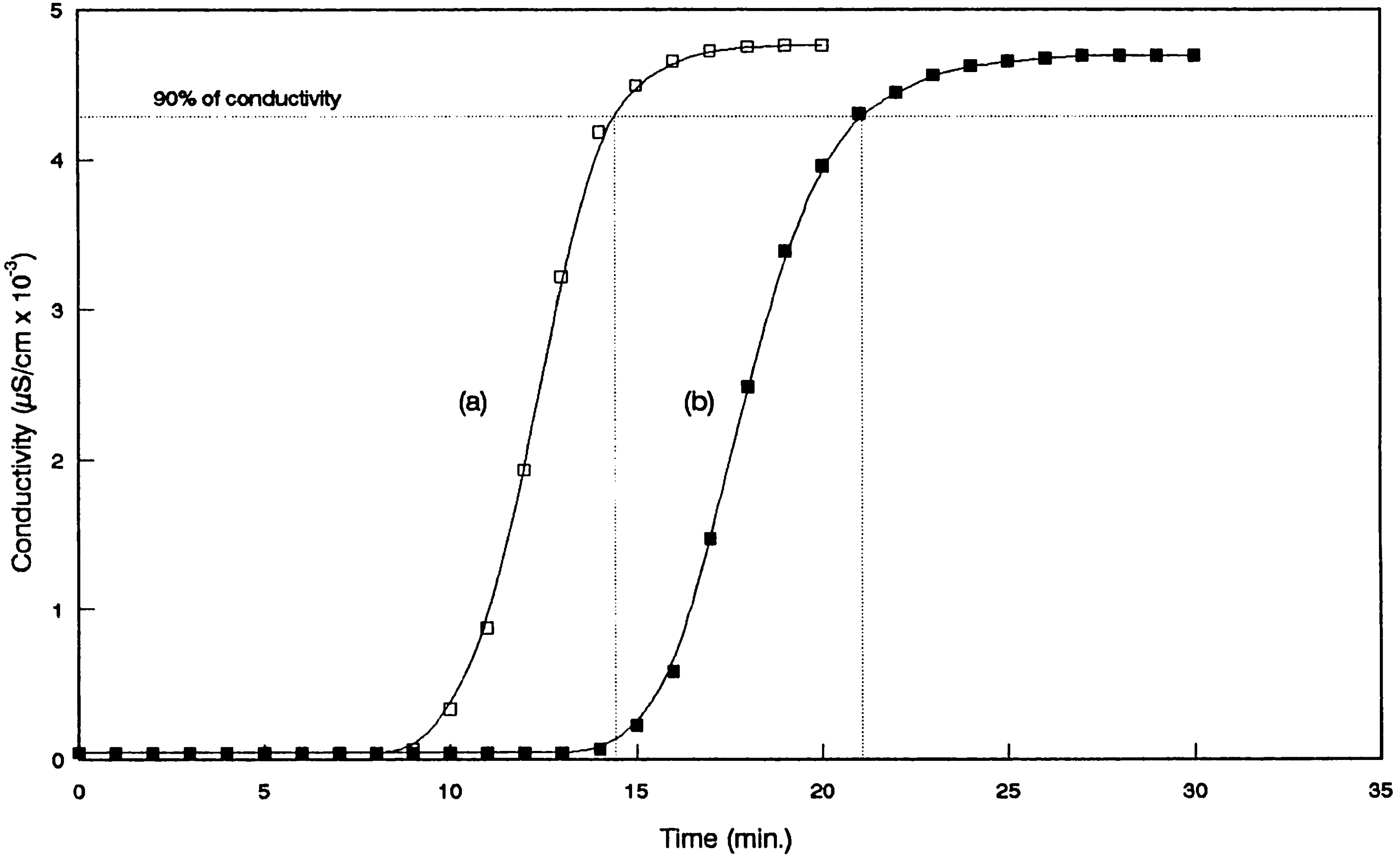


Figure 3.3: Residence time determination
(a) Flocculator (b) Flocculator + Filter

During the filtration run the head loss across the bed was monitored by means of the water manometers. Values of head loss were taken every 10 minutes from the 5th minute and also at 0, 60, 90 and 120 minutes (the latter when applicable).

The filter was operated at constant filtration rate of 111 ± 2 ml/min (approximately 1.5 mm/s filtration velocity). To control the rate and keep it constant as filtration took place, the filtrate flowmeter valve was gradually opened to compensate for the increasing resistance to flow due to clogging occurring within the filter bed.

To clean the filter bed for each experiment a total volume of 10 litres of 5% detergent solution (Decon 90, BDH, Poole) was pumped upwards through the filter inducing a bed expansion between 5% and 10%. The filter bed was then left in contact with the Decon solution for at least 4 hours before rinsing for 60 minutes by further backwashing using 40-50 litres of distilled water. After rinsing, the bed was brought down to its original level by reducing slowly the backwashing flow rate to zero.

In order to check differences in the uniformity of the filter bed due to re-packing after backwashing, the clean bed head loss was measured before each filtration experiment. The average values of the Carman-Kozeny constant (K_f) for the majority of the experiments are presented in table 3.2.

	K_f	
	Mean	SD(%)
Moderate colour (47 experiments)	5.06	5.2
High colour (50 experiments)	4.65	3.8

Table 3.2: Variation of Carman-Kozeny constant during clean bed filter measurements (approach velocity - 1.5 mm/s.)

The difference of the average values between the moderate and high colour filtration experiments reflects the effect of the removal and re-laying of the filter bed between the two groups of experiments. From the experimental values, and taking into account the variation in the water temperature throughout the experimental period, consistency in the filter bed structure was considered good.

3.2.3 Analysis

The colour intensity of raw, flocculated and filtrated water, in both jar and filtration tests, was determined using a spectrophotometer (Pye Unican SP8-100) at a fixed wavelength of 400 nm and 40 mm light path. As colour is pH-dependent, measurements reported, unless stated, were made at the constant pH value used in the filtration experiments.

For a number of experiments turbidity was also measured using a Hach 2100a Turbidimeter (Hach Chemical company, Iowa, USA).

After colour and turbidity measurements the raw and filtrate water samples (composite samples only) were acidified to pH<2 with nitric acid AnalaR grade and kept in the fridge for subsequent aluminium residual analysis. To determine the residual aluminium concentration Flameless Atomic Absorption (Atomic Absorption Spectrophotometer 603, Perkin-Elmer, Norwalk, Connecticut, USA) was used, and the procedure previously developed at Imperial College was followed (Carrondo et al., 1979).

3.2.4 Chemicals

The principal chemicals used were the water coagulants: Aluminium Sulphate analytical reagent grade ($Al_2(SO_4).16H_2O$ - BDH Chemicals, Poole) with 2% of impurities and 0.005% of insoluble matter, and Magnafloc LT 31 (Allied Colloids Ltd., Bradford) supplied as a solution containing 50% w/w of active content and described as 'containing polyamine'. Solutions of both chemicals were prepared by dissolving the necessary amount of the chemical in milli-Q water to obtain the desired concentration.

Solutions N/100 or N/10 of HCl and NaOH were used for pH correction. Other chemicals were also used as part of specific analysis, and these were always of analytical grade.

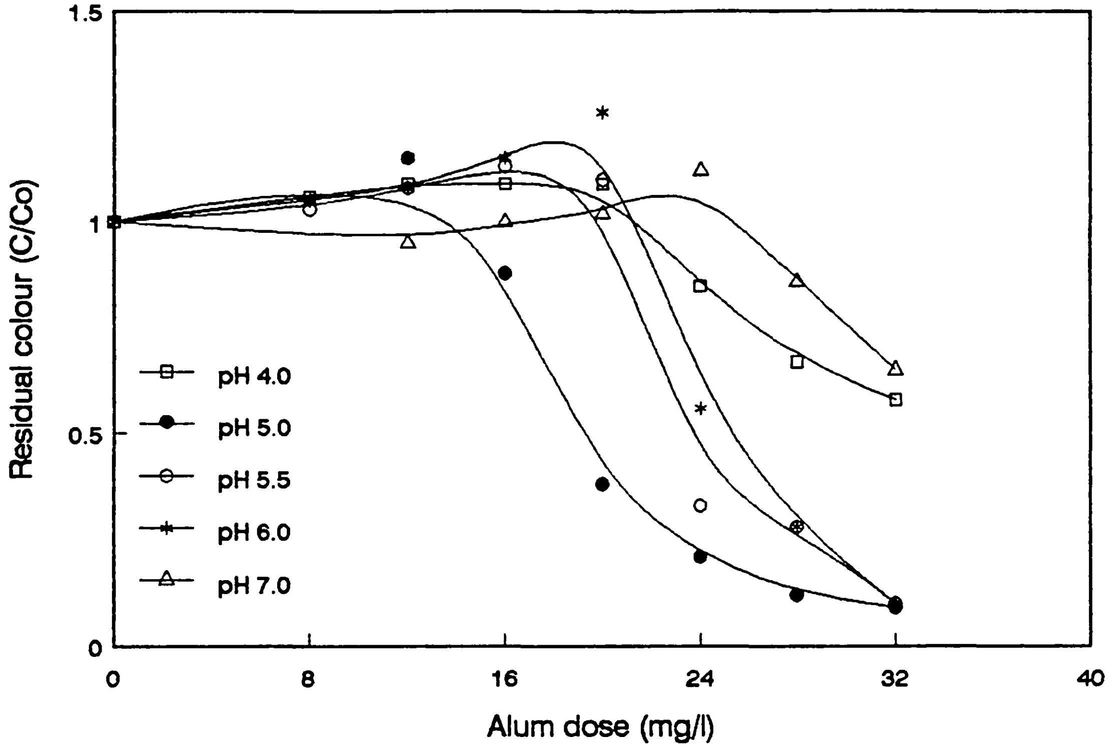
3.3 Results and discussion

3.3.1 Coagulation tests

The selection of the pH to be used in the direct filtration experiments was based on coagulation tests where only aluminium sulphate was used as coagulant. It is known that the efficiency of coagulation with aluminium salts is strongly affected by pH while with organic polyelectrolytes with strongly ionized groups are much less sensitive to pH changes (Gregory, 1978; Graham, 1982).

Figure 3.4 summarizes the results for colour removal obtained with the lower coloured water (2.5 Absorbance units/metre) at various pH values, the results are presented in two different ways to emphasize the effect of the pH. The general behaviour observed is very much in agreement with previous works (Black and Willems, 1961; Hall and Packham, 1965; Edzwald, 1979 and others). Good colour removals are achieved between pH 5 and pH 6, and slower and more incomplete extent of coagulation is observed at lower and higher pH values. The optimum pH for colour removal was found to be around pH 5 where the precipitation of flocs occurred at lower coagulant doses. However, a comparison of the residual colour profiles at pH 5 and pH 6 in figure 3.4 indicates that the optimum alum dose for both pH values tends to be very close.

The results in table 3.3 suggest that pH 6 is the best pH value in terms of residual aluminium concentration. Other investigators (Vik et al., 1985; Jackson et al., 1988) and full scale plant operator's experience have shown that the optimum pH for residual aluminium is slightly higher than the one for residual colour.



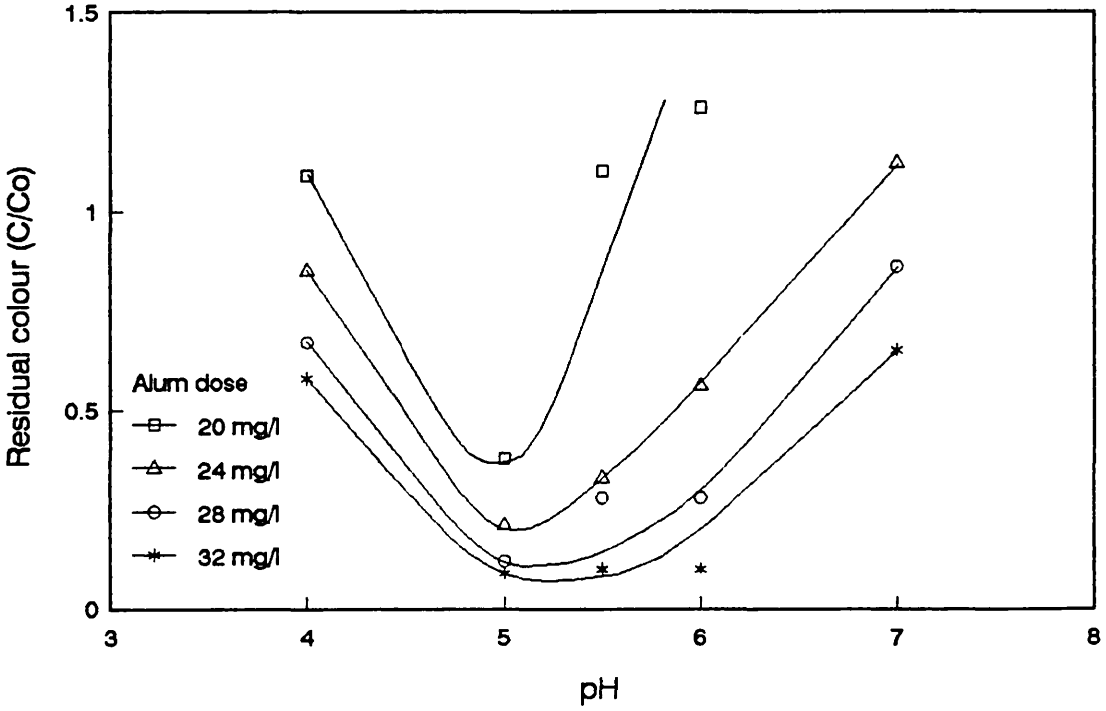


Figure 3.4: Jar test at various pH values

pH value	Residual aluminium (mg/l)	
	Alum dose - 28 mg/l	Alum dose - 32 mg/l
4.0	2.88	2.55
5.0	0.22	0.34
5.5	0.20	0.05
6.0	0.12	0.01
7.0	1.32	1.30

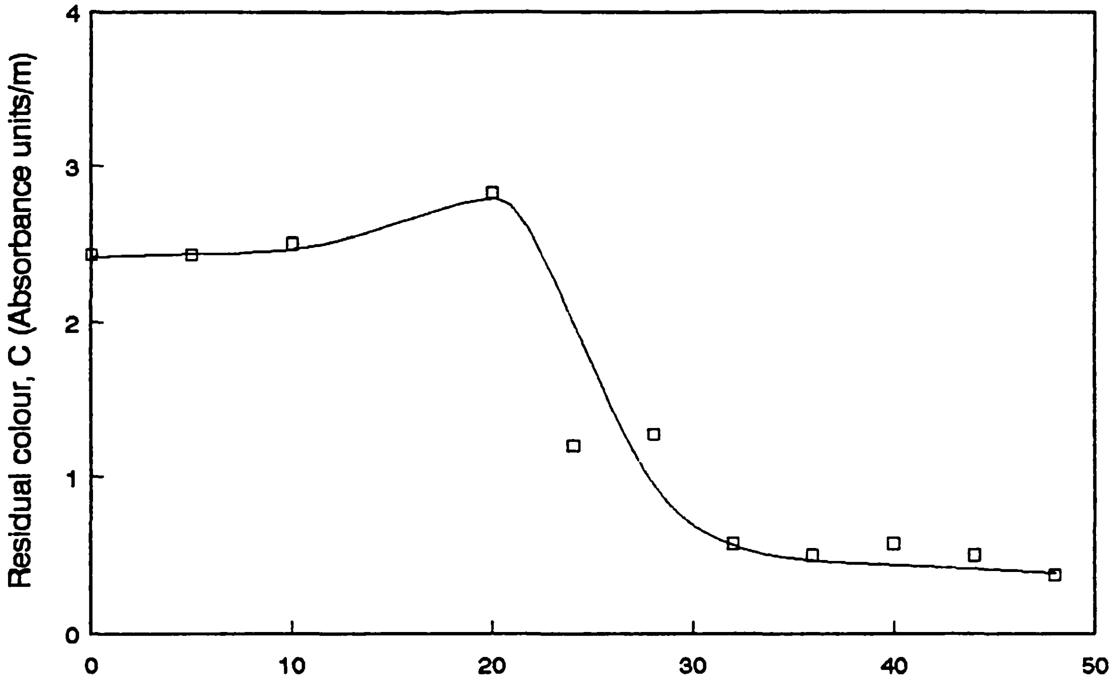
Table 3.3: Variation of residual aluminium with coagulation pH (jar test)

So, taking into account both colour removal and the concentration of residual aluminium, pH 6 was selected to be used in the following stages of the experimental work.

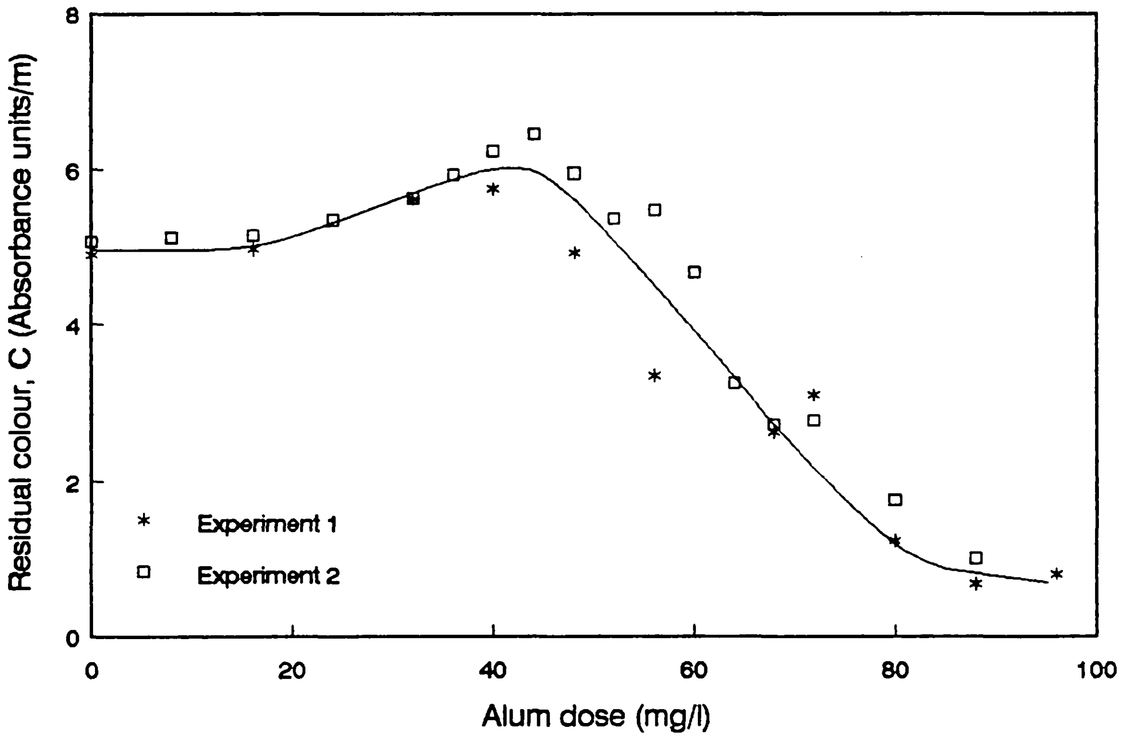
Further coagulation tests were carried out with the objective of investigating the range of coagulant doses to be covered in the filtration experiments. The jar tests were performed at pH 6 and with the moderate coloured (2.5 Absorbance units/metre) and high coloured (5 Absorbance units/metre) reconstituted waters, using both alum and polymer (Magnafloc LT 31) as primary coagulants.

The results obtained using alum as sole coagulant are presented in figure 3.5. From these results the optimum dose of 32 mg/l of alum (2.7 mg/l as Al) can be selected for the moderate coloured water and for the highly coloured water an optimum dose around 80 mg/l of alum (6.9 mg/l as Al) can be suggested despite the degree of scattering in the experimental data.

Although very similar in shape, the two curves are not entirely proportional. The deviation from stoichiometry that is observed can probably be explained by the fact that for each situation different mechanisms of coagulation are involved. According to Dempsey et al. (1984) between pHs 5 and 6 the predominating reaction depends on the



(a) Moderate coloured water



(b) High Coloured water

Figure 3.5: Jar test with alum at pH 6

applied aluminium dose, such that at low aluminium doses the humic material may be precipitated mostly by polymeric aluminium hydrolysis species, while at higher doses the removal of humic material occurs by adsorption of the humics, or soluble humic-aluminium complex, on precipitated aluminium hydroxide.

In the coagulation experiments with polymer as sole coagulant the jar test procedure described in section 3.2.1 was altered to avoid filtering solutions containing polymer. Instead, at the end of the slow mixing period the samples were centrifuged for 15 minutes at 3000 rpm. Also, additional turbidity measurements of the flocculated and centrifuged waters were carried out and, together with absorbance readings, were used in the evaluation of the coagulation performance.

The polymer coagulation was characterized by the lack of any visible flocs and the high opacity of the flocculated water. According to Narkis and Rebhun (1975) the observed turbidity (opacity) is due to the formation of a colloidal precipitate resulting from the reaction between a cationic polymer and the anionic humic substances. The lack of visible flocs, on the other hand, indicates that the aggregation of the colloidal precipitate into large flocs was not effective, probably due to the diluted nature of the humic solution and the lack of turbidity in the raw water.

The results obtained for the moderate and high coloured waters are shown, respectively, in figures 3.6 and 3.7. It can be observed that the residual ratio profiles for turbidity and absorbance measurements (T/T_o* and C/C_o*) follow the same trend despite the differences in behaviour of the data for the coagulated water (T_o* and C_o*) . The differences in absolute values are due to the fact that the nephelometric turbidity is based upon the measurement of the scattered radiation at a right angle to the incident bean of light, while the absorbance is a measurement of the diminution of power of a collimated beam as a result of scattering by the particles present in solution. However, when the results are treated relatively (clarified/coagulated ratio) the differences are eliminated and both parameters exhibit the same trend.

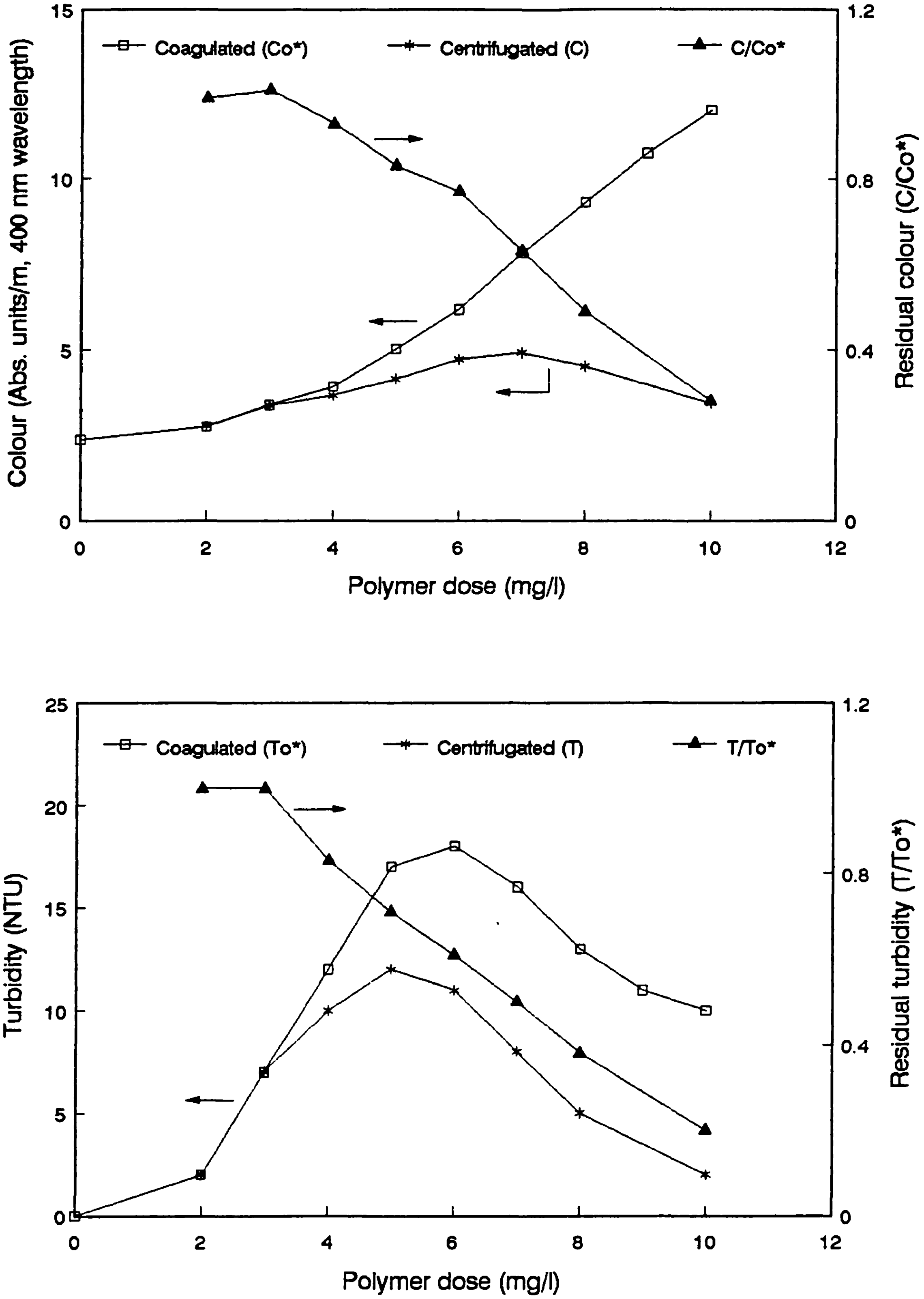


Figure 3.6: Jar test with polymer - Moderate coloured water

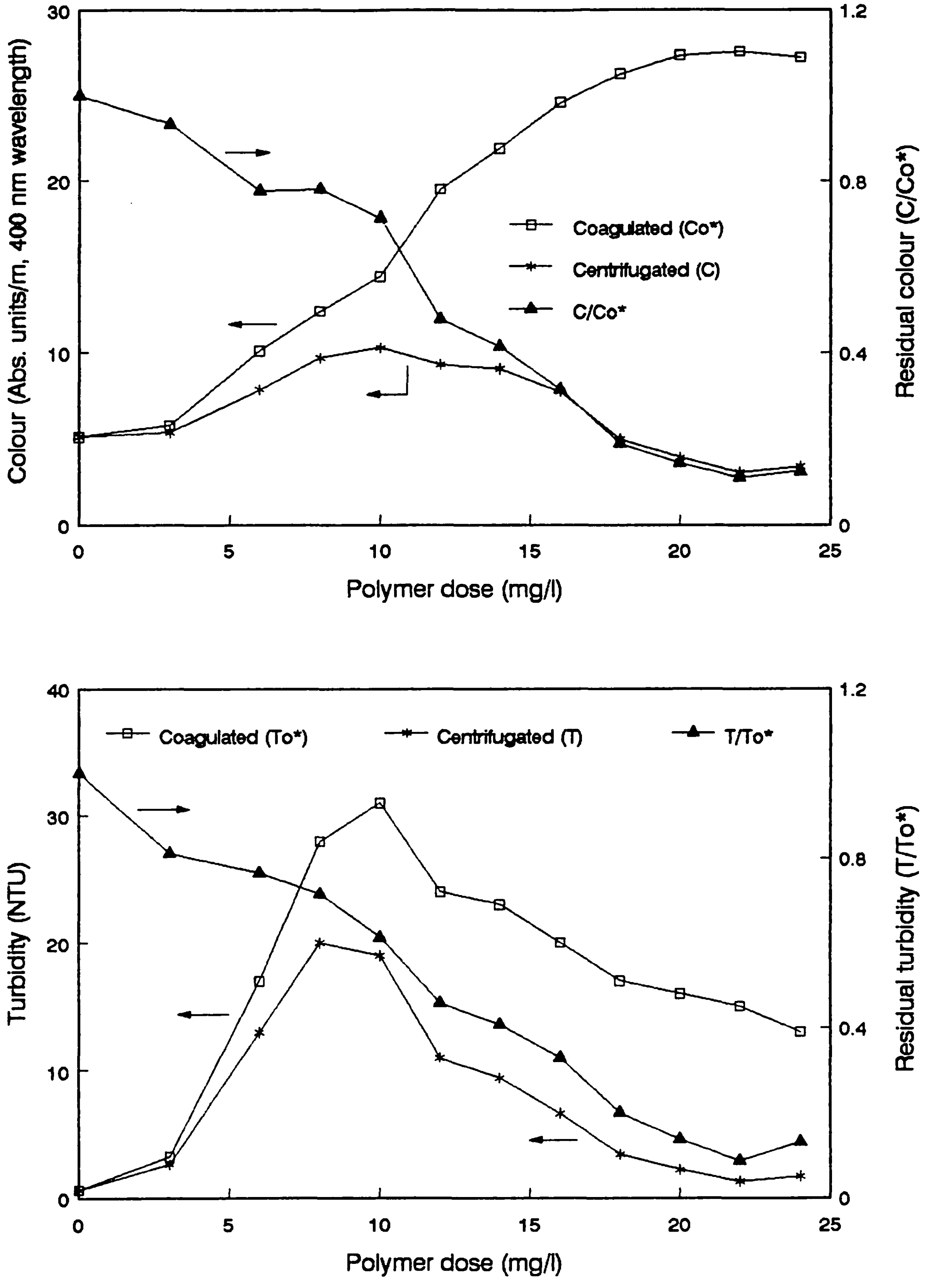


Figure 3.7: Jar test with polymer - High coloured water

The optimum polymer dose for each coloured water is not clear. The removal ratio curves suggest that in the range of doses studied the increase of polymer dose leads to a continuous improvement in the removal of the precipitate by centrifugation. However, it should be noted that for the high coloured water a decrease in removal is observed at 26 mg/l of Magnafloc LT 31. These results will be discussed later in the light of the floc size determinations.

3.3.2 Filtration tests

All the filtration experiments were carried out at pH 6, using only reconstituted coloured water prepared from Washburn extracted material. For each of the filtration tests the apparatus used and procedure followed was that described in section 3.2.2 and the filter was operated at a constant filtration rate of approximately 1.5 $mm^3/mm^2.s$ (5.3 $m^3/m^2.h$).

Initially, filtration experiments were performed with the moderate coloured water (2.5 absorbance units/metre). A series of filtration tests using alum as sole coagulant was carried out to determine the optimum coagulant dose based on filtration performance. From this specific value the alum dose was then systematically reduced to zero and, at each aluminium dose, filtration experiments were carried out for various polymer dosages. Thus, a filtration performance matrix was produced for a number of alum-polymer combinations.

The same procedure was followed for the high coloured water (5 absorbance units/m) allowing a second filtration performance matrix to be generated.

The effect of pre-treatment, i.e. different combinations of alum and polymer, on the filtration performance was evaluated using the Ives' Filterability Number (Ives, 1978). The Filterability Number (*F*) is one of the various numerical indices proposed in the literature to evaluate filter performance (see table 3.4) and according to Janssens and co-workers (1982, 1986) it appears to be the more appropriate to assess optimum operating conditions.

The Filterability Number is dimensionless and relates the filterability of a suspension to the filter material taking into account clarification, clogging and flow rate. It is defined by Ives as:

$$F = \frac{H\,(C/C_o)}{vt} \tag{1}$$

Where H is the head loss (water gauge)

C is the average filtrate quality

C_o is the inlet suspension quality

v is the approach velocity

t is the time of filter run

For good filtration a low head loss and a low filtrate concentration is desired as well as a long time of operation. Consequently, a good filterability is expressed by a low filterability number value. It is important to note, however, that the actual numerical value of F has no significance by itself but relative values of F are significant. A rule of thumb is 'the lower the filterability number the better the filtration'.

The main parameter selected to express the water quality in the calculation of the filterability number F was the colour intensity. The average filtrate colour, C, was measured from the so called composite samples. As the precise meaning of 'C_o' in Ives equation is not clear in the present context, two values could be used as inlet quality in this work, (i) the raw water apparent colour (before coagulant addition) which was a constant value dependent only on the raw water colour concentration, here designated as C_0, or (ii) the apparent colour of the flocculated solution entering the filter, here designated as C_0*. Calculations performed using both definitions showed that, although the filterability number values differ significantly depending on which definition is adopted, there is a close similarity in the variation of F values with coagulant dosages.

Index definition	Reference
Filter Performance Index $FPI = \dfrac{vt}{H}$	Gamet and Redemacher (1959)
Filterability Index $FI = \dfrac{\lambda\sigma}{\Delta H}$	Cleasby (1969)
Solids Captured Index $SCI = \dfrac{(C_o - C)vt}{H}$	Biskner and Young (1977)
Modified Filterability Index $MFI = \dfrac{H}{\Delta H_1 \, \Delta C_1 \, (C_o - C)vt}$ $\Delta H_1 = (H_{lim} - H)/H_{lim}$ $\Delta C_1 = (C_{lim} - C)/C_{lim}$	Lekkas (1977)
Filterability Number $F = \dfrac{H(C/C_o)}{vt}$	Ives (1978)

Table 3.4 : Filter performance indices (after Janssens, 1982)

Where ΔH is head loss for a given layer and time interval

H_{lim} and C_{lim} are respectively the available head loss and permissible filtrate quality

λ is the filtration coefficient

σ is the specific deposit

Taking this into account and considering that the use of the performance ratio C/C_o* emphasizes the part played by the filter in the process train, the results presented here are always related to the influent apparent colour C_o*.

Moderate coloured water

In the first phase of the work, when the lower colour concentration was used, a filtration run time of 120 minutes was adopted. For each filtration run the filtrate quality and head loss were monitored over this time as previously described (section 3.2.2.2).

Figures 3.8 to 3.12 show the results of individual filtration tests grouped according to the coagulation conditions investigated. The results of the filtration tests where alum-polymer combinations were used are presented in figures 3.9 to 3.11 as complete sets of experiments at each constant alum dose. Figure 3.8 and 3.12 show the results of filtration obtained when alum and polymer were respectively used as sole coagulant. From these figures the following observations can be made:

(i) In the experiments where aluminium sulphate was used as sole coagulant a consistent trend of rising head loss and improving colour removal was observed as higher doses of alum were added. It should be noted, though, that increasing the alum dose above 32 mg/l (2.7 mg/l as Al) did not produce substantial improvements in colour reduction but conversely underdosing significantly worsened colour removal. These results followed the same trend observed in the jar test results (figure 3.5 a).

(ii) Generally a similar pattern was followed in the experiments where alum-polymer combinations were used. Initially, when alum was added alone or combined with low doses of polymer, little or no increase in head loss occurred and the filtrate quality was poor.

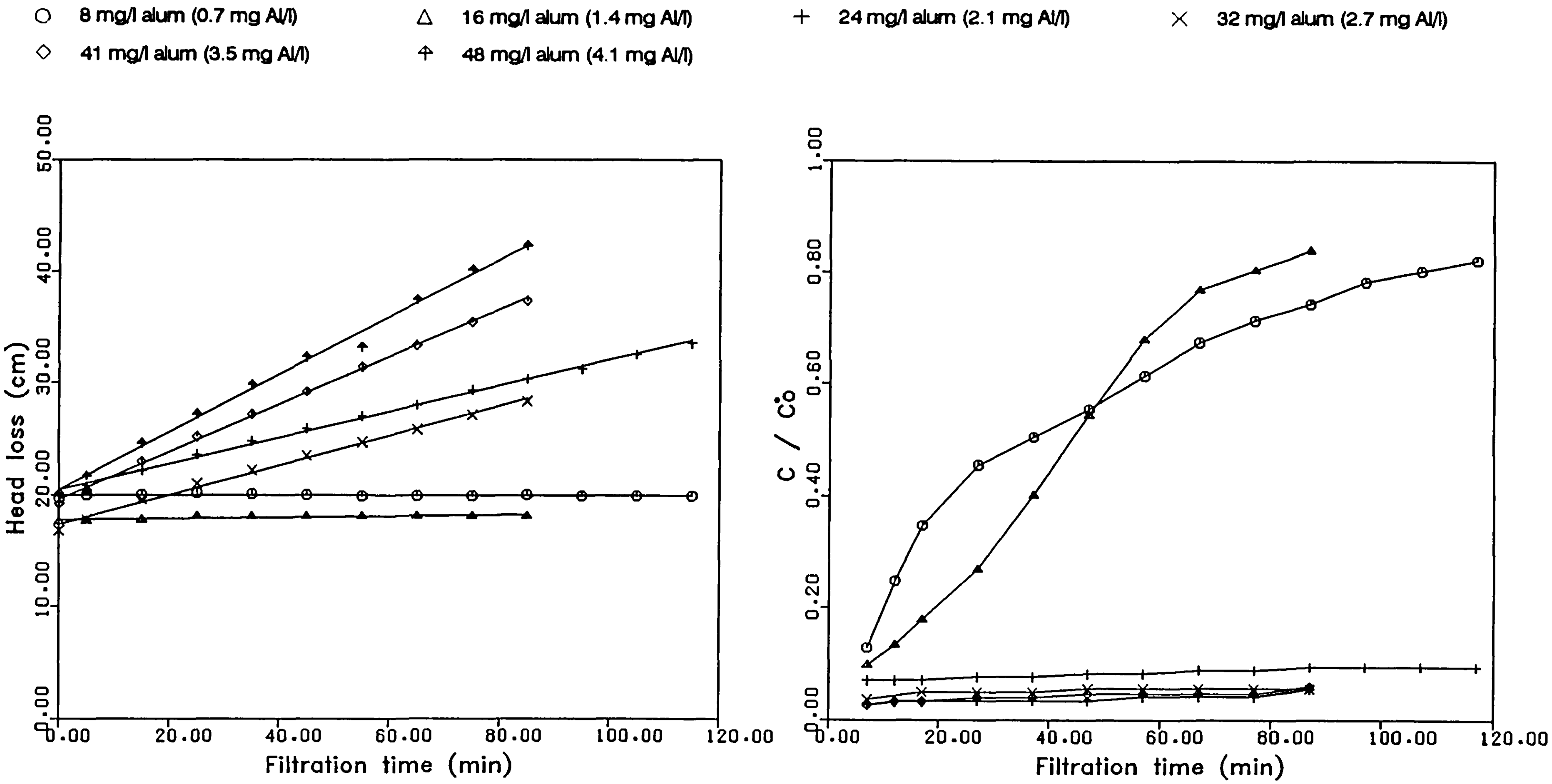


Figure 3.8: Filtration tests - Moderate coloured water (2.5 Abs. units/m)

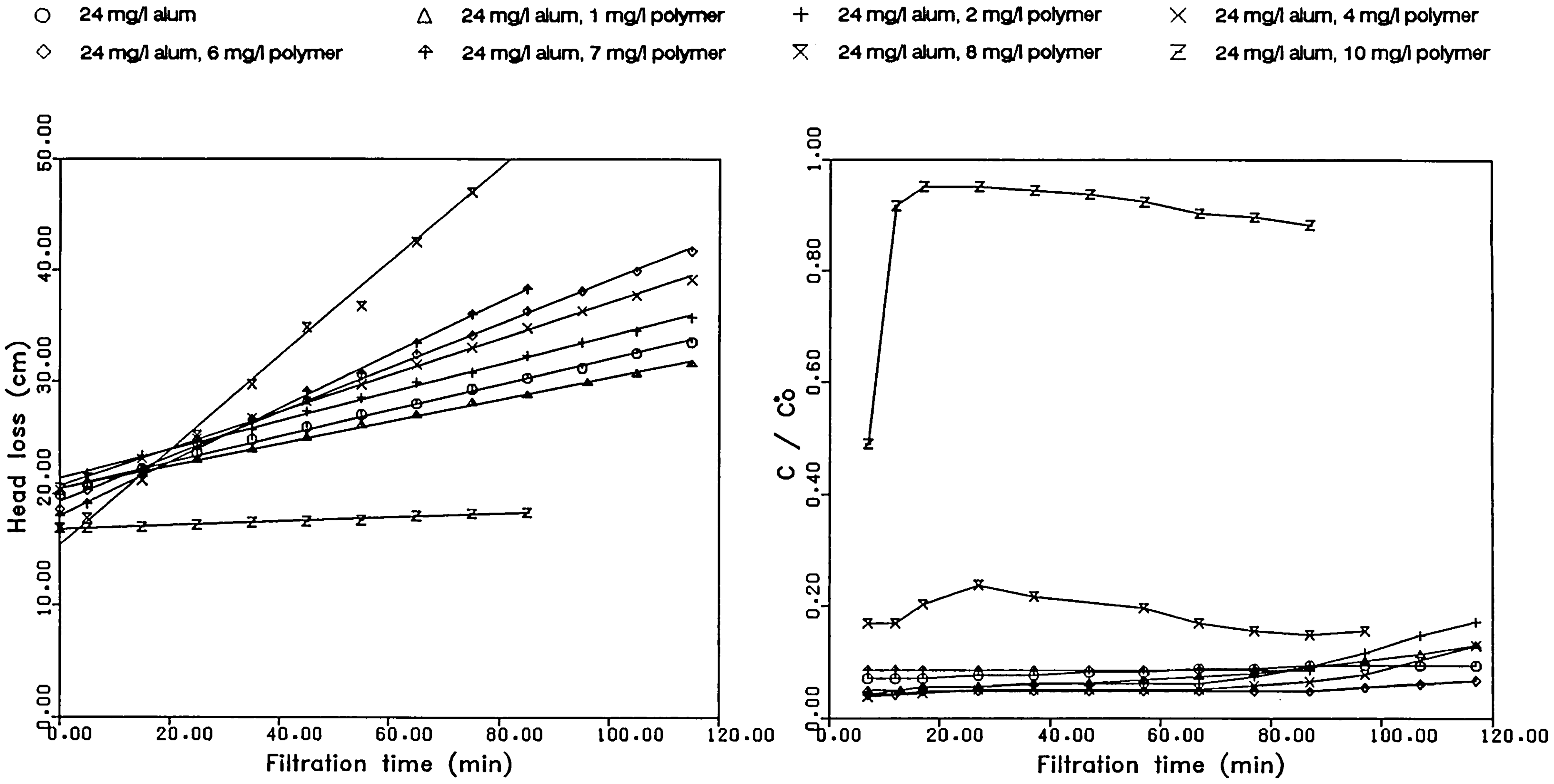


Figure 3.9: Filtration tests - Moderate coloured water (2.5 Abs. units/m)

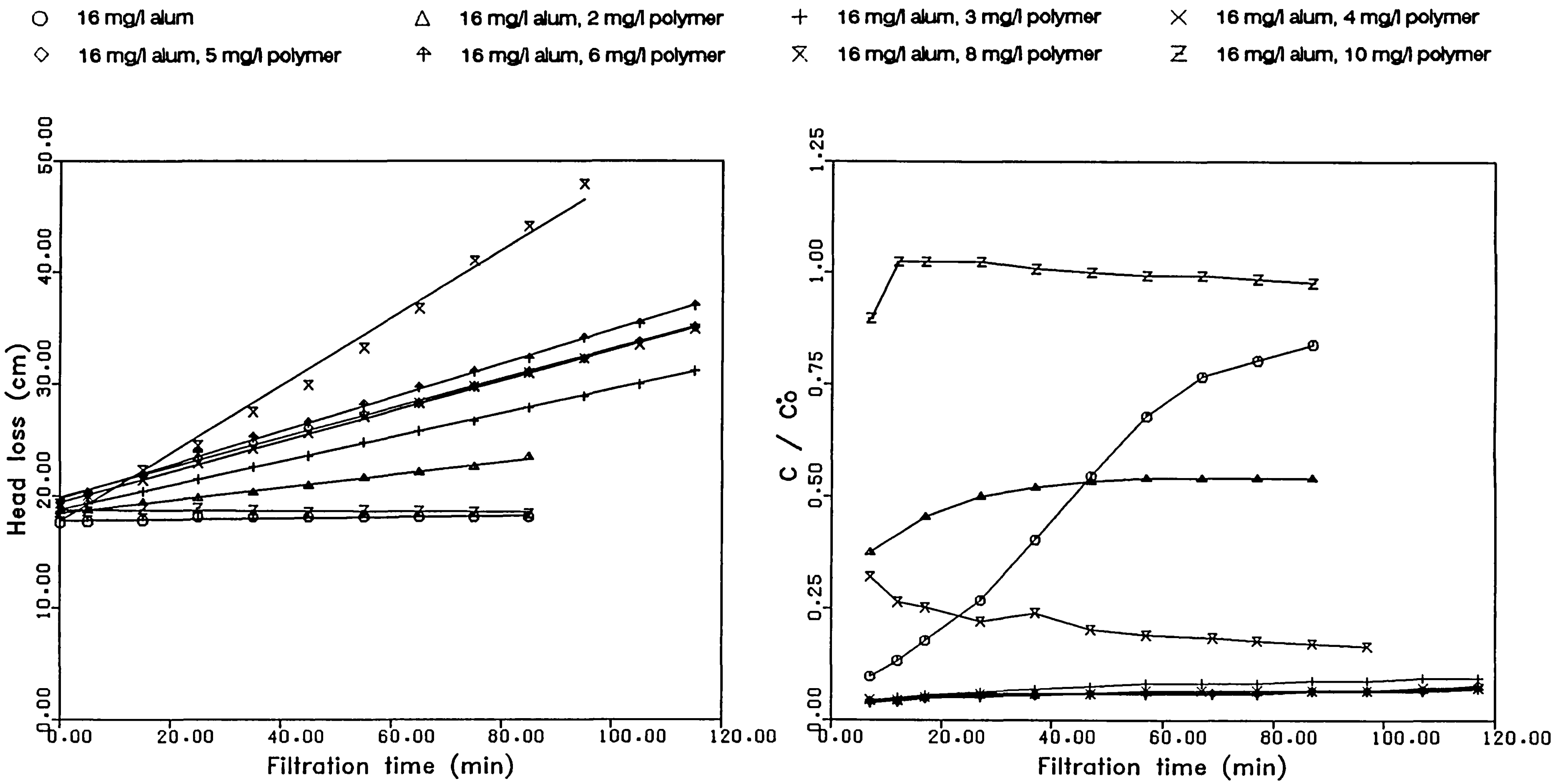


Figure 3.10: Filtration tests - Moderate coloured water (2.5 Abs. units/m)

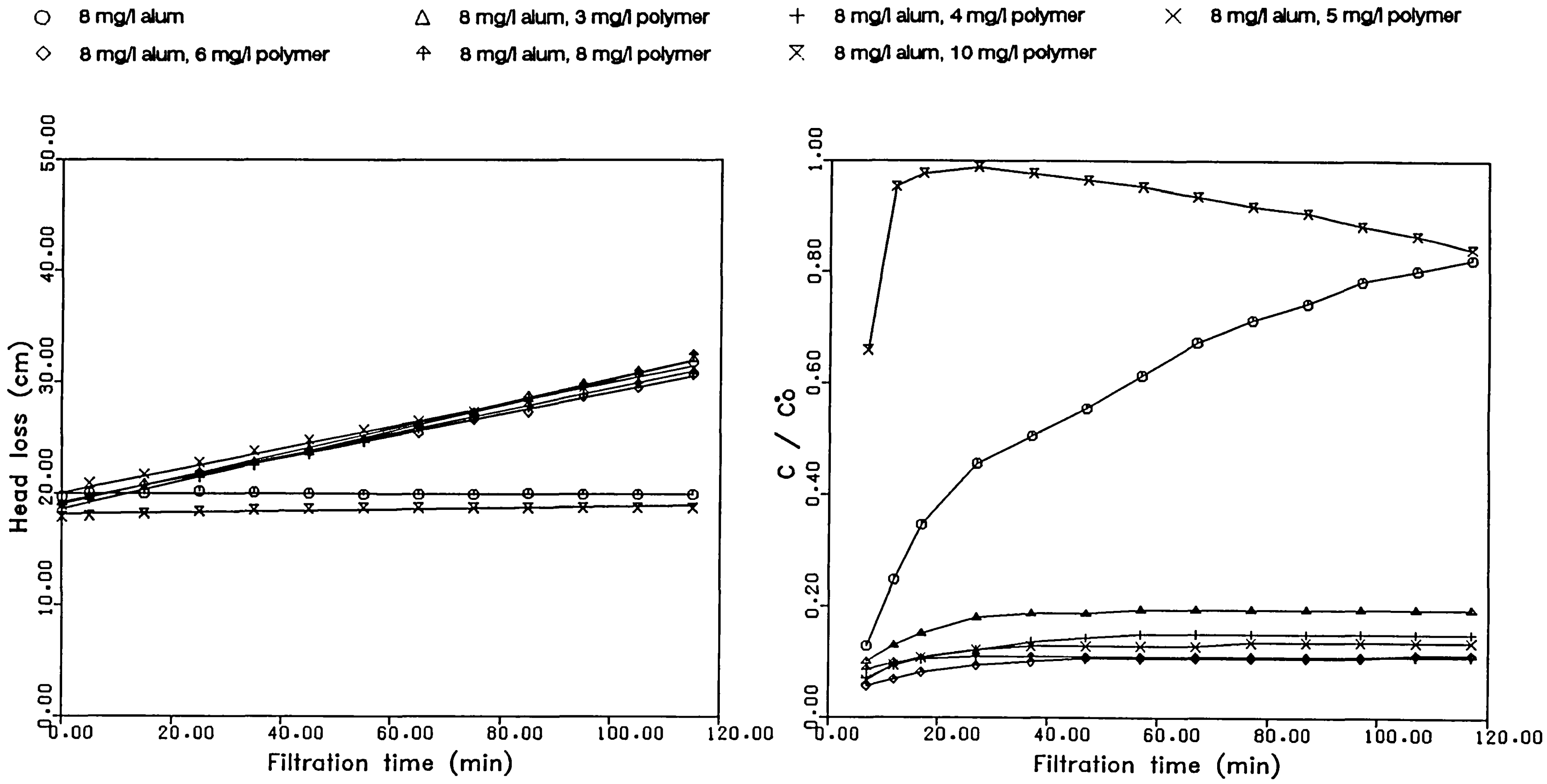


Figure 3.11: Filtration tests - Moderate coloured water (2.5 Abs. units/m)

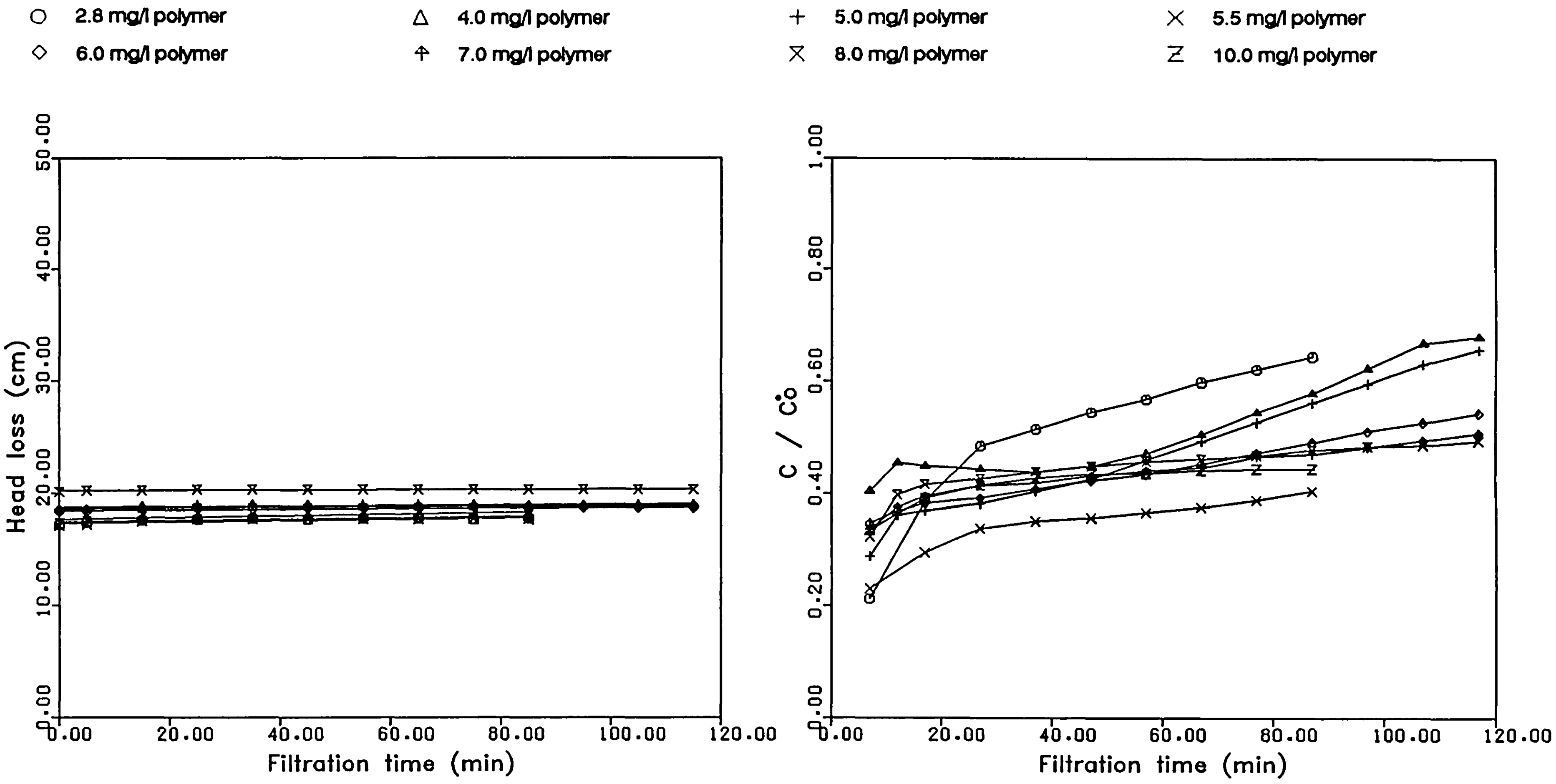


Figure 3.12: Filtration tests - Moderate coloured water (2.5 Abs. units/m)

Further increase in polymer dose led to a systematic increase in the rate of head loss development and to an improvement in the quality of the filtrate, up to a point where the addition of higher polymer doses resulted in the degradation of the quality of the filtered water. The initial phase of little head loss development and poor filtrate quality becomes less evident with the increase of the alum dose component of the combination, disappearing at 24 mg/l of alum.

(iii) Very inefficient filtration was observed when the polymer was used as sole coagulant. Although some colour removal is apparent there was no measurable head loss development indicating none or very little particle retention within the filter bed. As in the jar test visible flocs were not formed after the flocculation period, but the 'flocculated' water was always characterized by high turbidity.

The behaviour of the residual turbidity relative to the turbidity of the flocculated water in the present filtration tests was very similar to that of the residual colour as exemplified in figure 3.13. This close similarity is due to the fact that the turbidity present in the flocculated water was associated with the coagulation of the humic substances, since the raw coloured water was virtually free of turbidity.

The effect of the various coagulation conditions on the utilization of the filter bed was analyzed by measuring the head loss across the bed at various filtration times. Figure 3.14 show some typical results. From these, and other similar results obtained at different alum-polymer combinations, it could be observed that in the vast majority of the filtration experiments the clogging front did not reach the bottom layer of the filter bed, and that more than a third of the total head loss occurred in the first 8 centimetres of the filter bed (15% of the total depth). The increase in polymer dose, at a given alum concentration, led to a systematic increase in both total head loss and

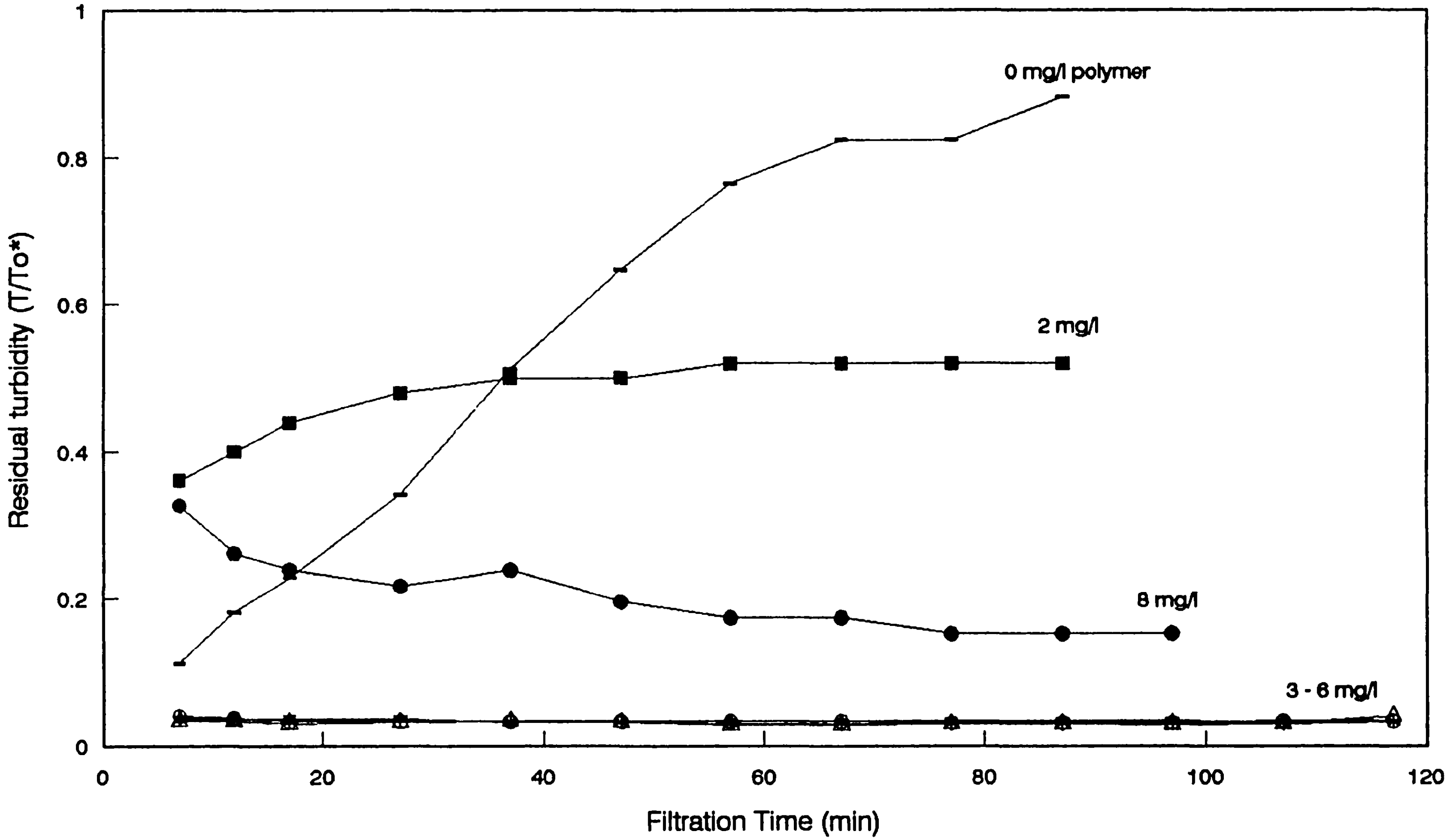
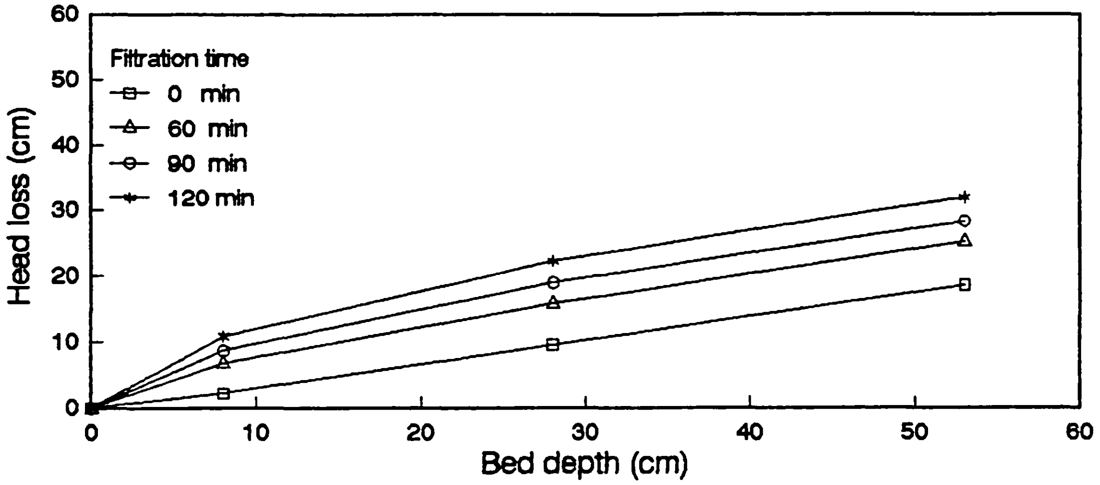
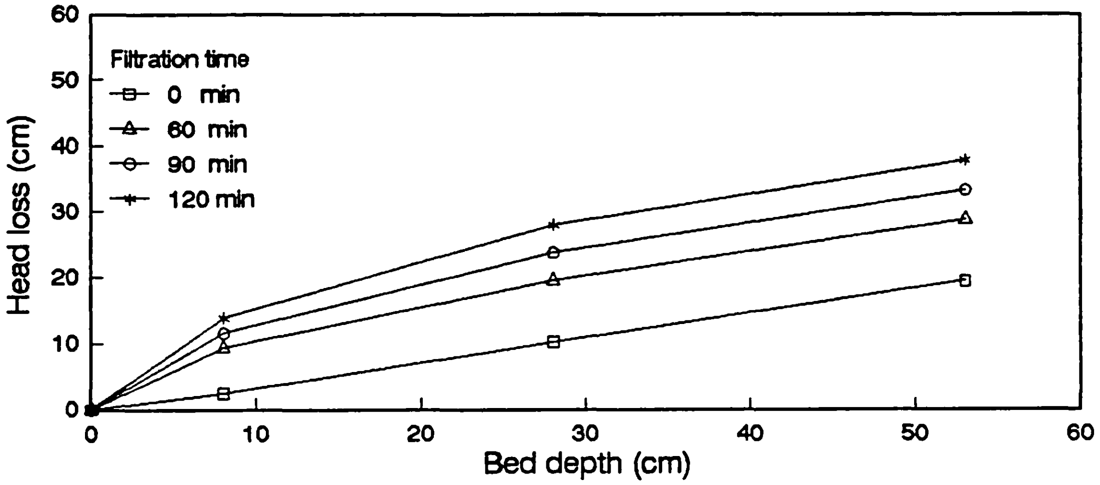


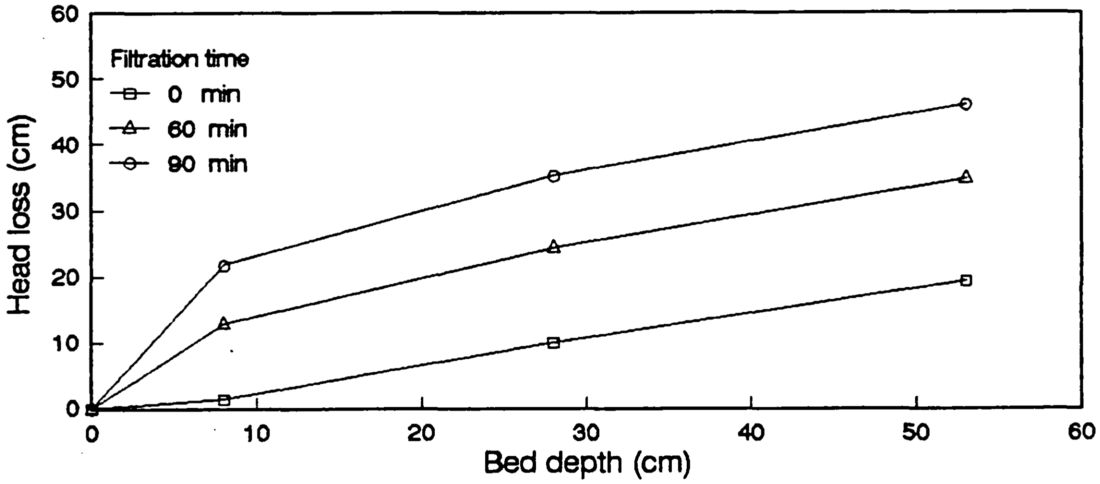
Figure 3.13: Filtration tests - Turbidity removal (typical example)
Moderate coloured water - Alum 16 mg/l + Polymer



16 mg/l alum + 3 mg/l polymer



16 mg/l alum + 6 mg/l polymer



16 mg/l alum + 8 mg/l polymer

Figure 3.14: Head loss across the filter bed at various filtration times (typical example)

the deposit accumulated on the top layer of the bed. However, it is interesting to note that the head loss development became less sensitive to changes in polymer dose as the alum dose component of the combination decreased.

For each filtration test performed the filterability number was calculated at 3 different times - 60, 90 and 120 minutes - according to equation 4. From these calculations, it was observed that in the majority of the filtration experiments the numerical value of *F* decreases with the increase of filtration time. Moreover, the variation of *F* with the coagulants doses follows the same pattern regardless the time used in its calculation (e.g. figure 3.15). This behaviour results from the fact that the filtrate quality (C/C_0*) remained relatively constant throughout the filtration and the head loss varied linearly with time.

The performance of the filtration experiments with the moderate coloured water, expressed as the filterability number *F* calculated at 90 minutes of filtration time, is summarized in figure 3.16. It can be seen that for each set of experiments the variation in filterability number follows very closely the variation in the removal ratio, C/C_0* (figures 3.8 to 3.12), indicating the greater importance of this factor compared with the head loss in the resulting value of filterability number. The selection of an optimum dose based on these results will be examined later.

High coloured water

In the second phase of the filtration experiments the high colour concentration was used. Initially the same filtration run time used for the moderate coloured water was adopted, but after some experiments a strong tendency to an early breakthrough was observed and the filtration time was then reduced to 90 minutes.

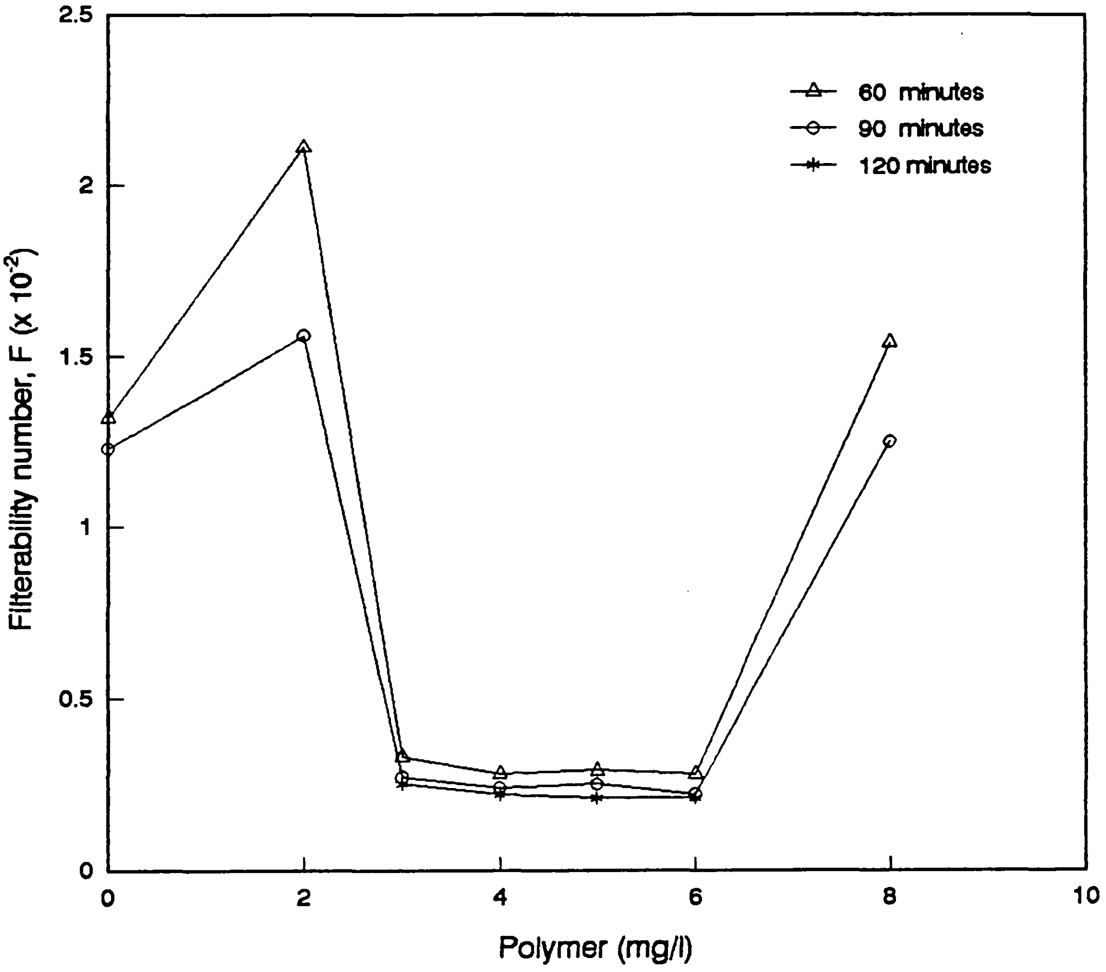


Figure 3.15: Filterability number calculated at various times

Moderate coloured water - Alum 16 mg/l + Polymer

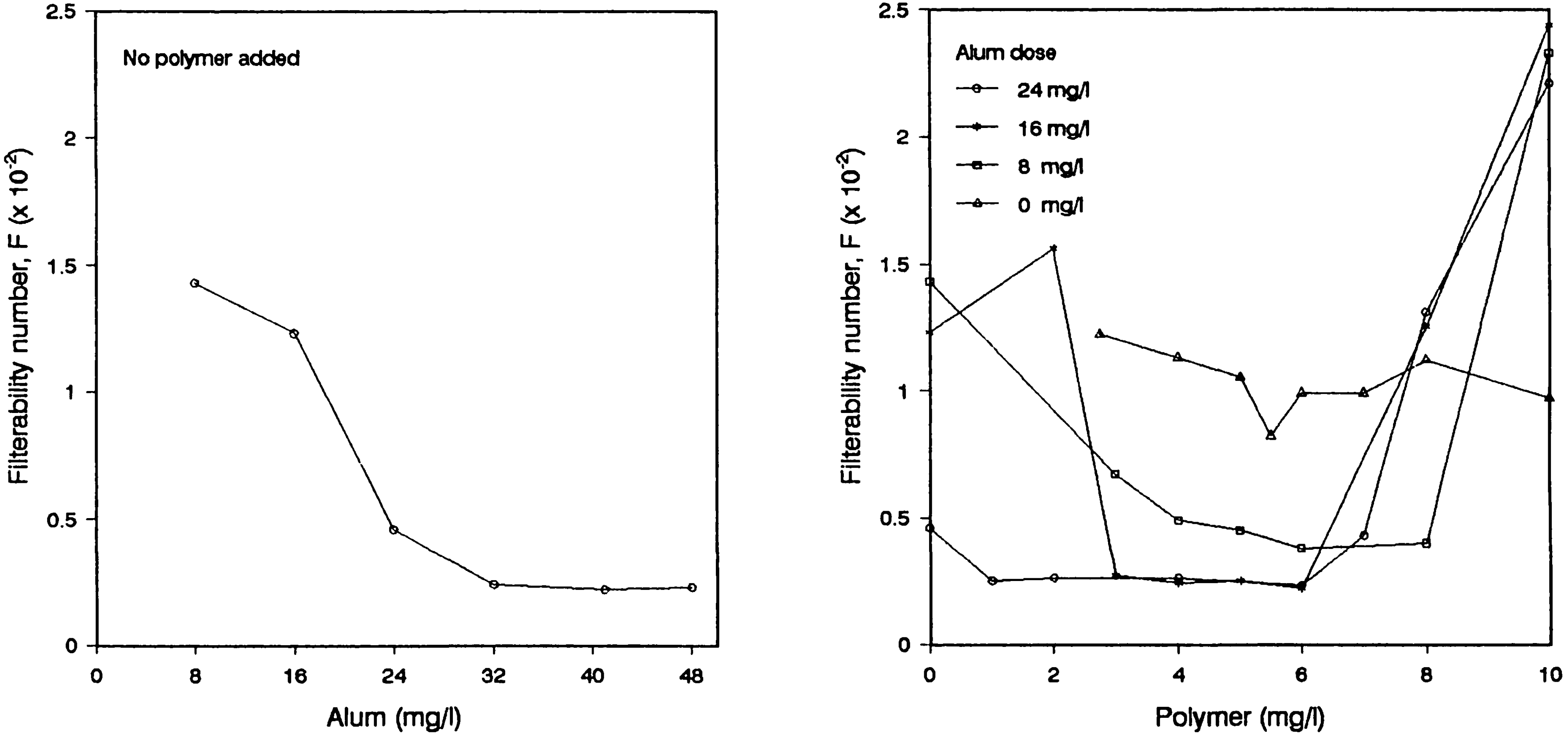


Figure 3.16: Filtration tests - Filterability number at 90 minutes

Moderate coloured water

Figure 3.17 to 3.23 present the results of individual filtration tests grouped according to the coagulation conditions studied. For those tests where alum-polymer combinations were used (figures 3.18 to 3.22), the results are presented as complete sets of experiments at each constant alum dose. The general behaviour of these filtration experiments is similar to that observed in the filtration tests with the lower coloured water, apart from the fact that quality breakthrough occurs within 90 minutes in most of the experiments.

The analysis of the head loss development across the filter bed throughout the filtration time showed that, again, the majority of the head loss was accumulated in the top portion of the bed (8 cm). However, in contrast with the previous observations (moderate colour), these results indicate that the clogging front generally reaches the bottom of the filter bed (e.g. figure 3.24), which is in agreement with the filtrate quality profiles. In other words, when the clogging front reaches the bottom of the filter the quality breakthrough occurs.

The filtration tests using polymer as sole coagulant were not completed in view of the poor results obtained with the two experiments done (figure 3.23) and their strong similarity with the results presented in figure 3.12.

Similarly to the previous experiments the filterability number was calculated at 60 and 90 minutes, as well as 120 minutes for those tests where the filtration time was that long. However, since for many filtration tests quality breakthrough occurs before the 60th minute, an additional *F* value was calculated at an arbitrary time (37 min) so that a pre-breakthrough condition was observed in all filtration experiments.

The filterability numbers calculated at 37, 60 and 90 minutes are shown in figures 3.25 to 3.27. As can be observed, when breakthrough occurs the variation of *F* with the filtration time does not follow the same behaviour observed for the lower coloured water (i.e. the *F* value decrease with the increase of time), reflecting the rapid degradation of the filtrate quality. At very low alum doses the breakthrough does not occurs before 90 minutes and therefore the *F* number behaves as for the water with moderate colour.

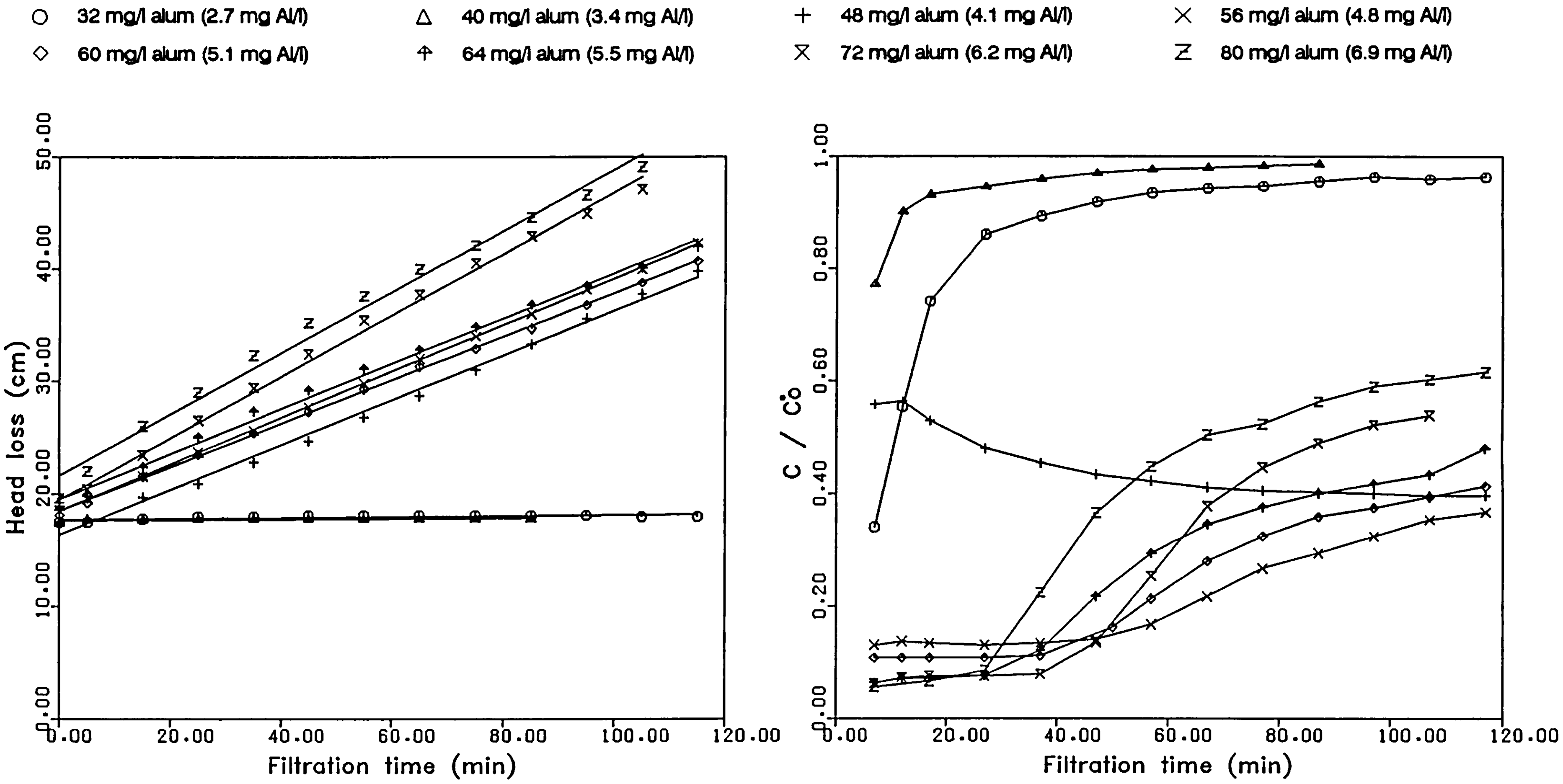


Figure 3.17: Filtration tests - High coloured water (5 Abs. units/m)

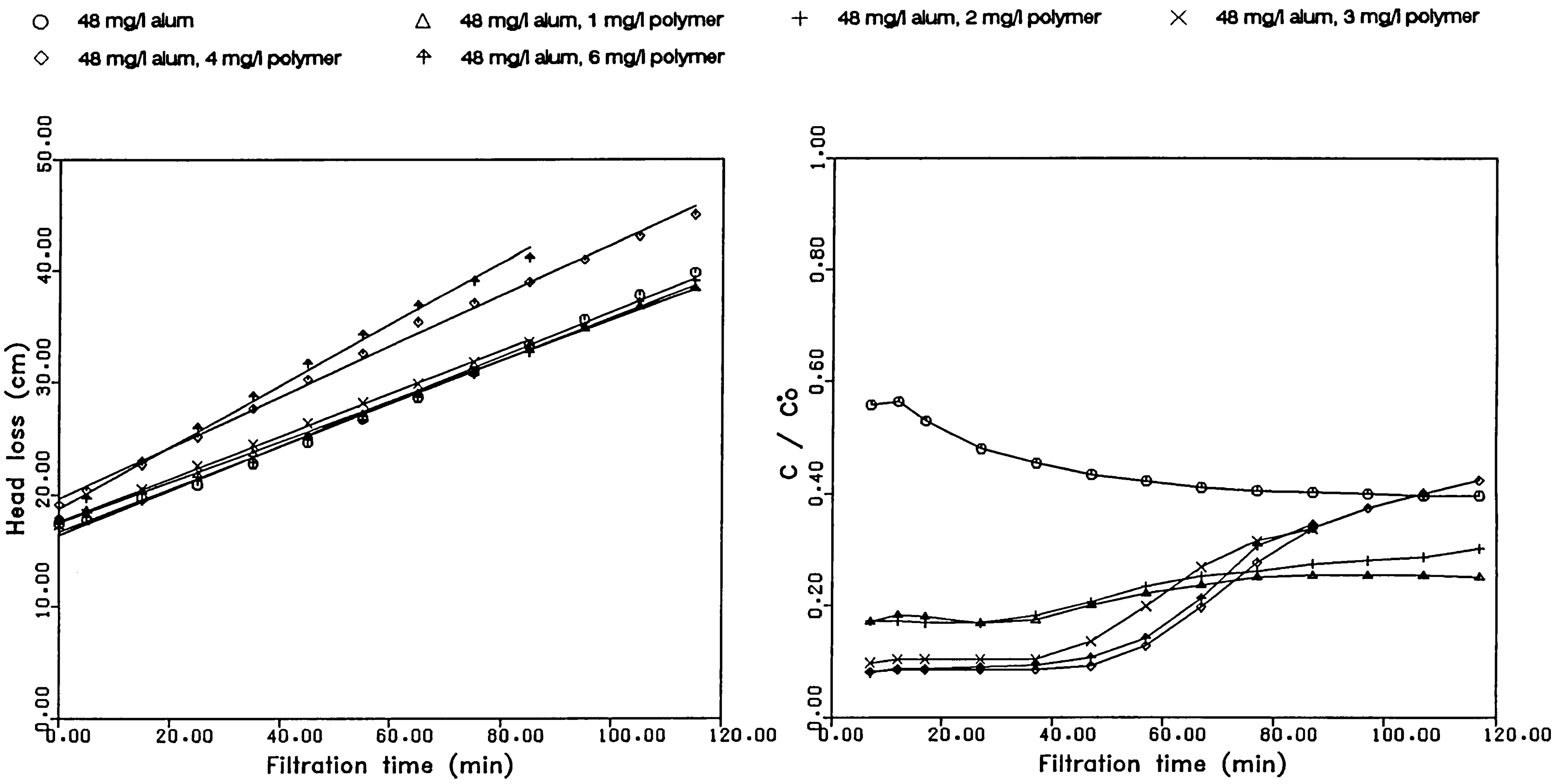


Figure 3.18: Filtration tests - High coloured water (5 Abs. units/m)

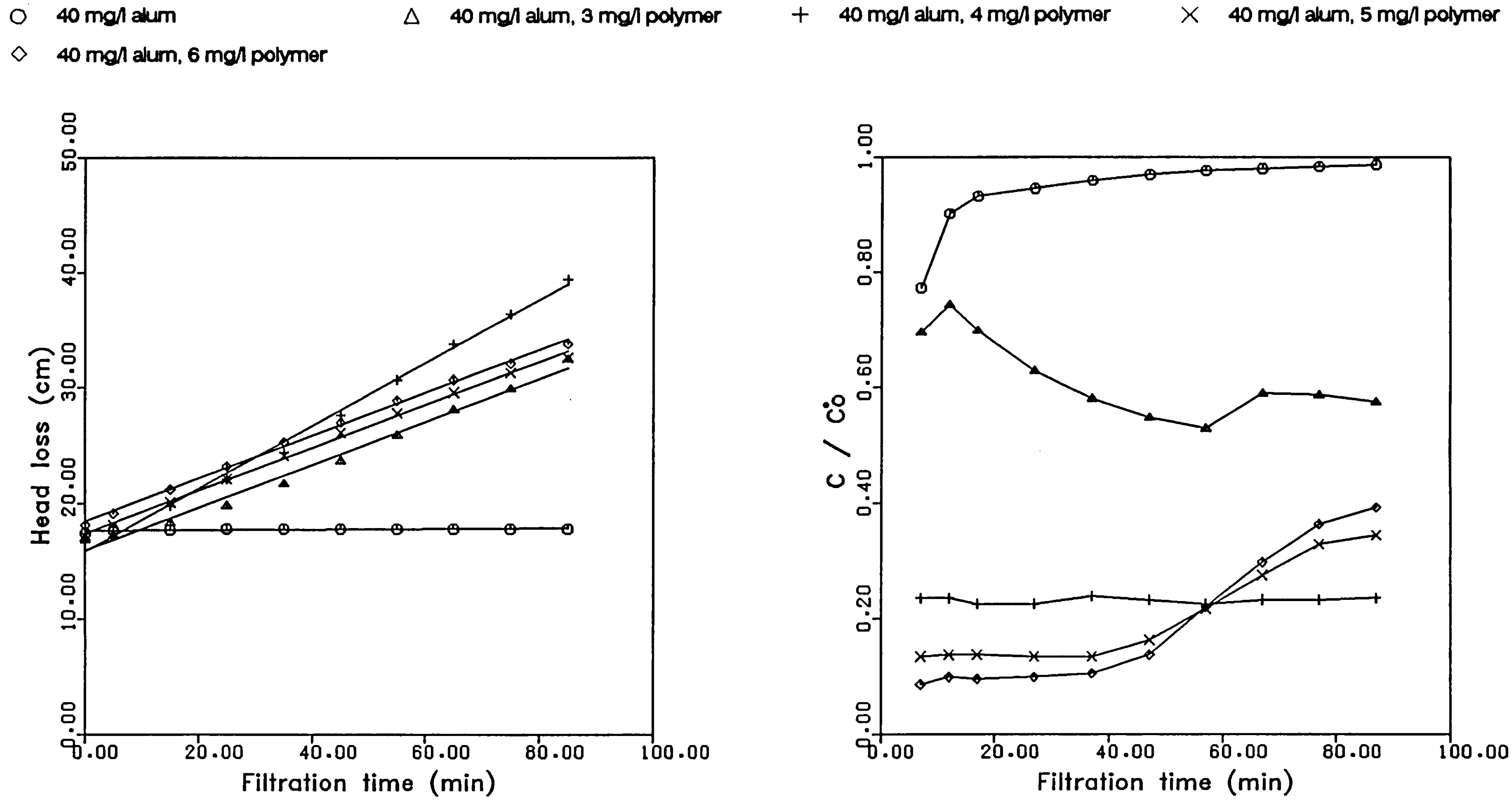


Figure 3.19: Filtration tests - High coloured water (5 Abs. units/m)

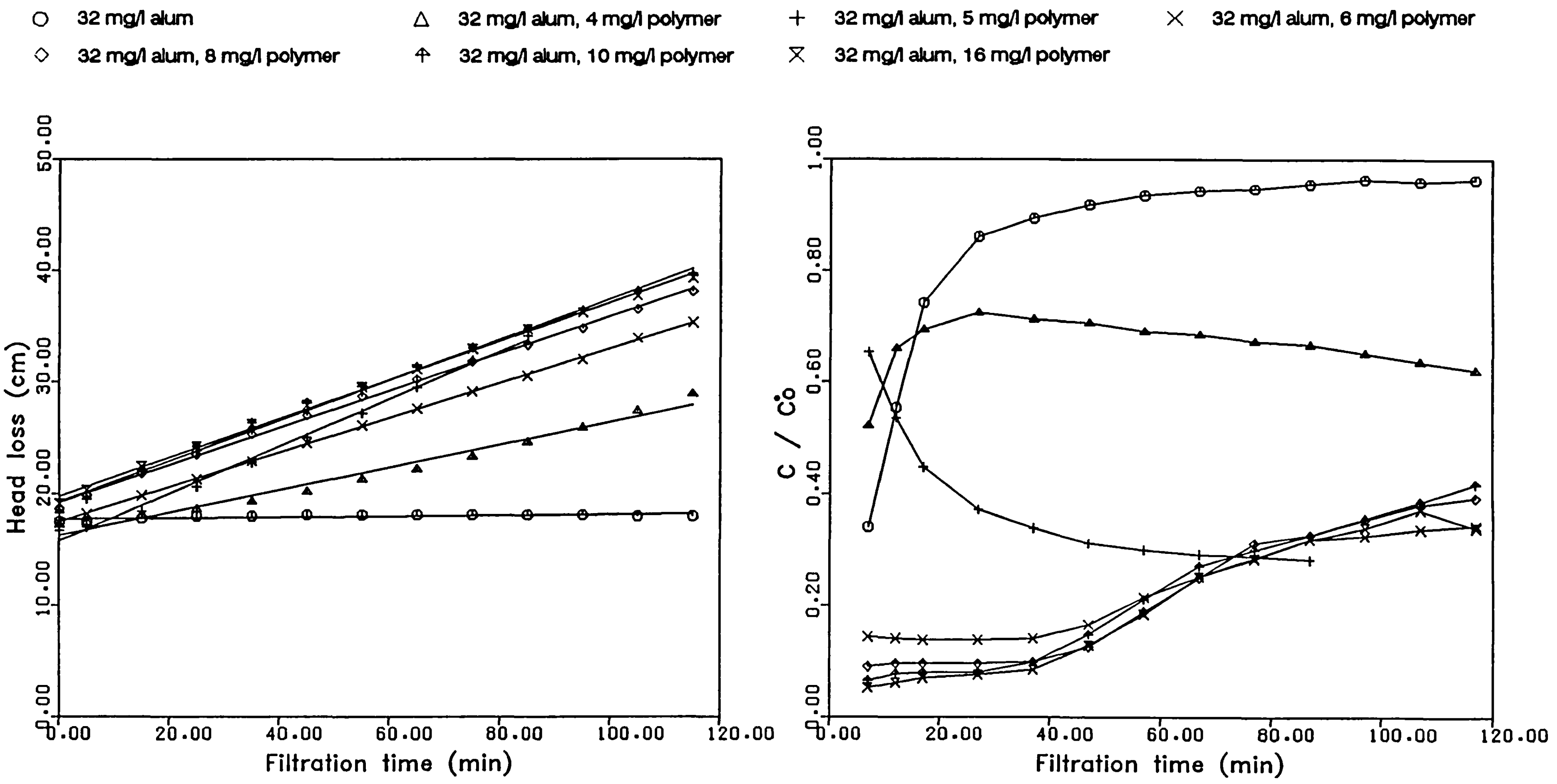


Figure 3.20: Filtration tests - High coloured water (5 Abs. units/m)

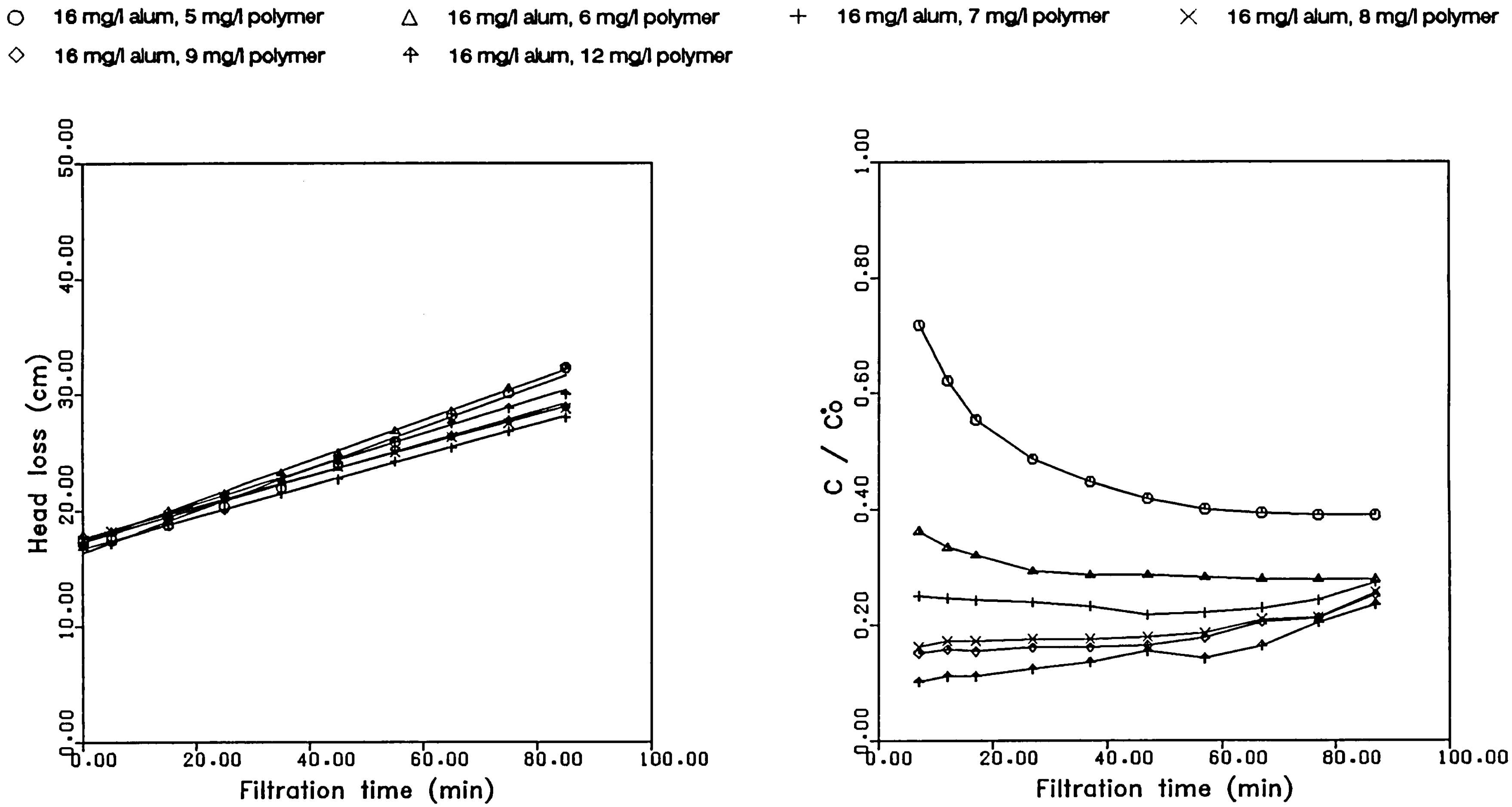


Figure 3.21: Filtration tests - High coloured water (5 Abs. units/m)

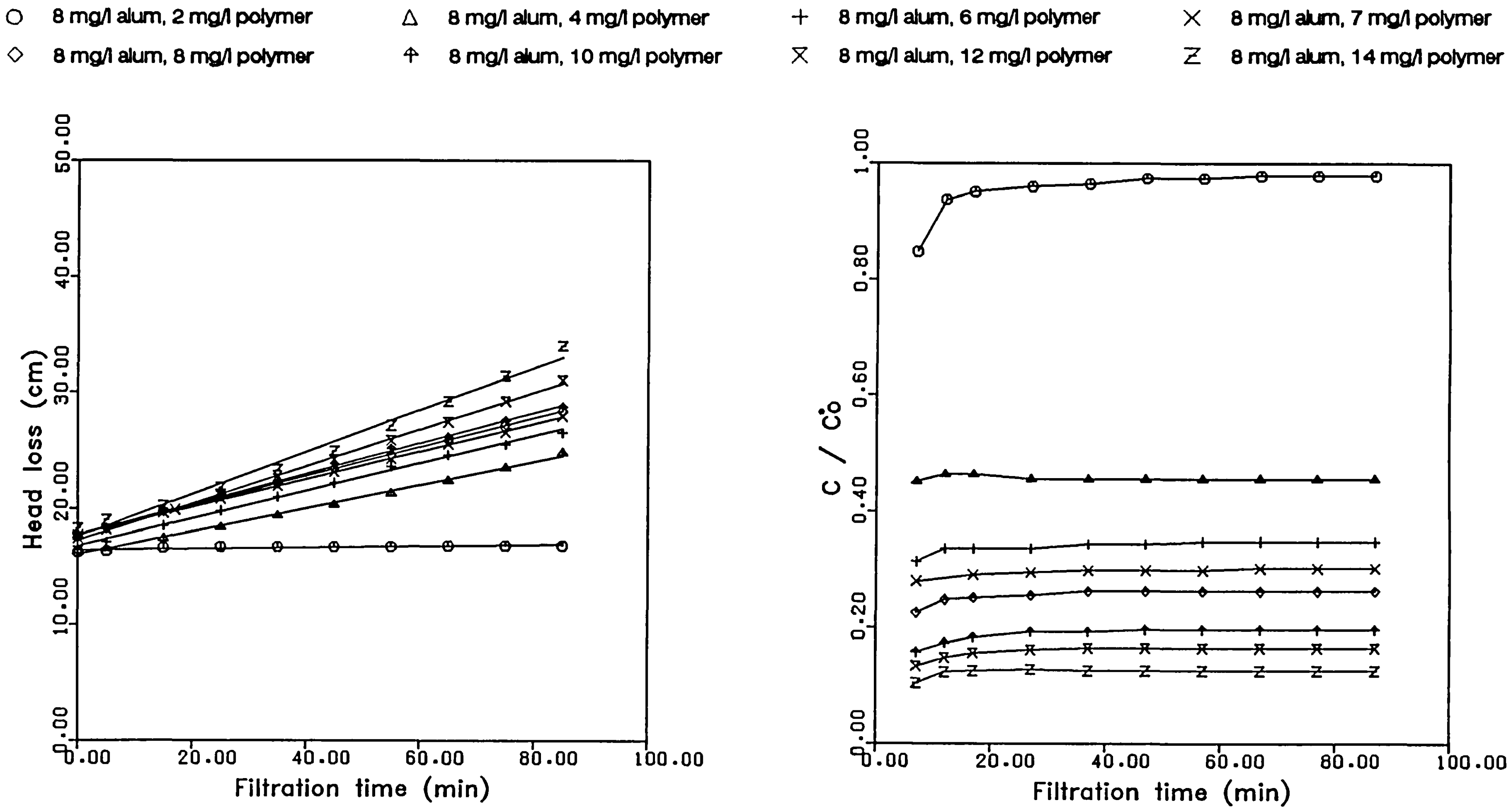


Figure 3.22: Filtration tests - High coloured water (5 Abs. units/m)

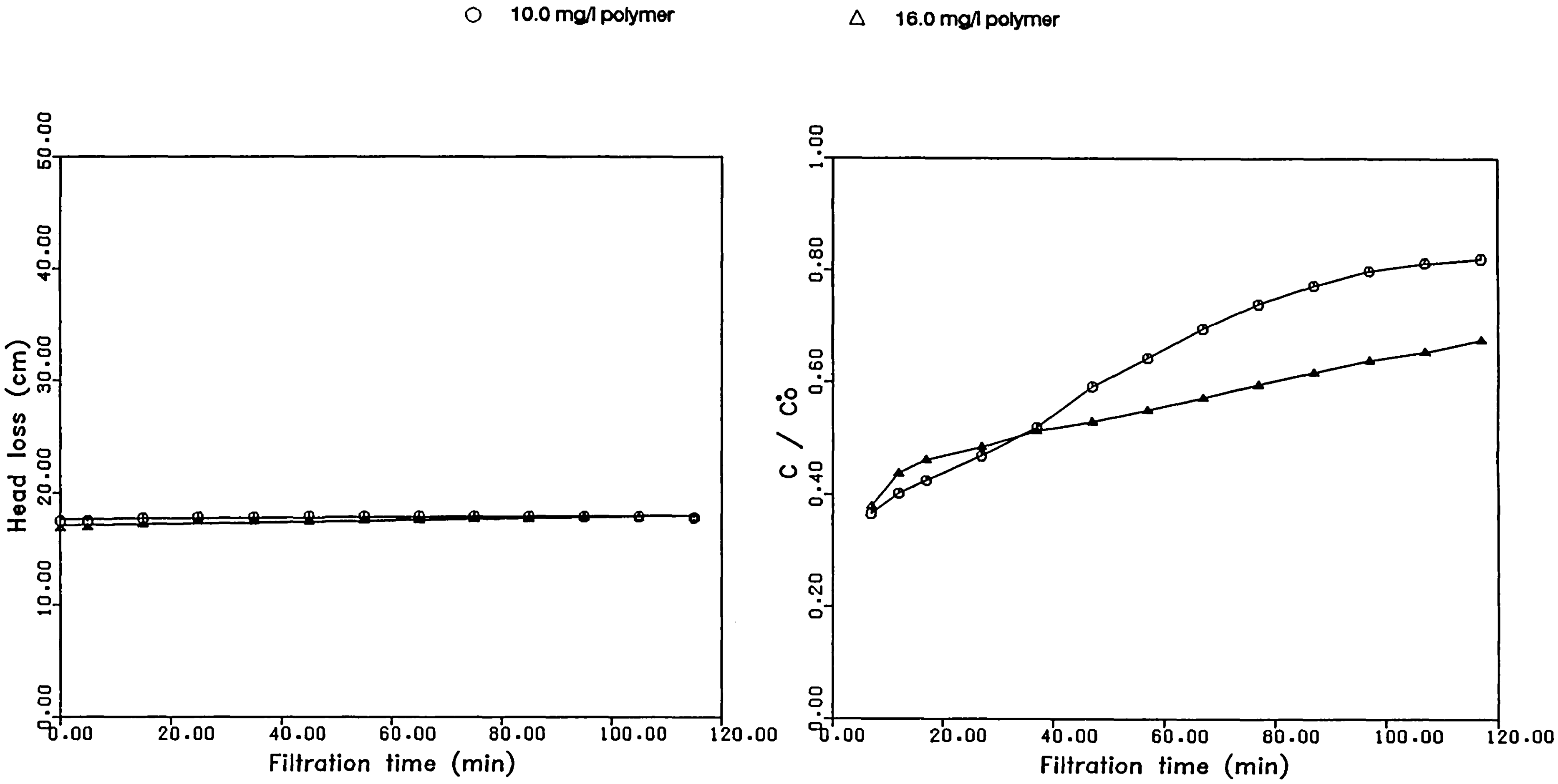
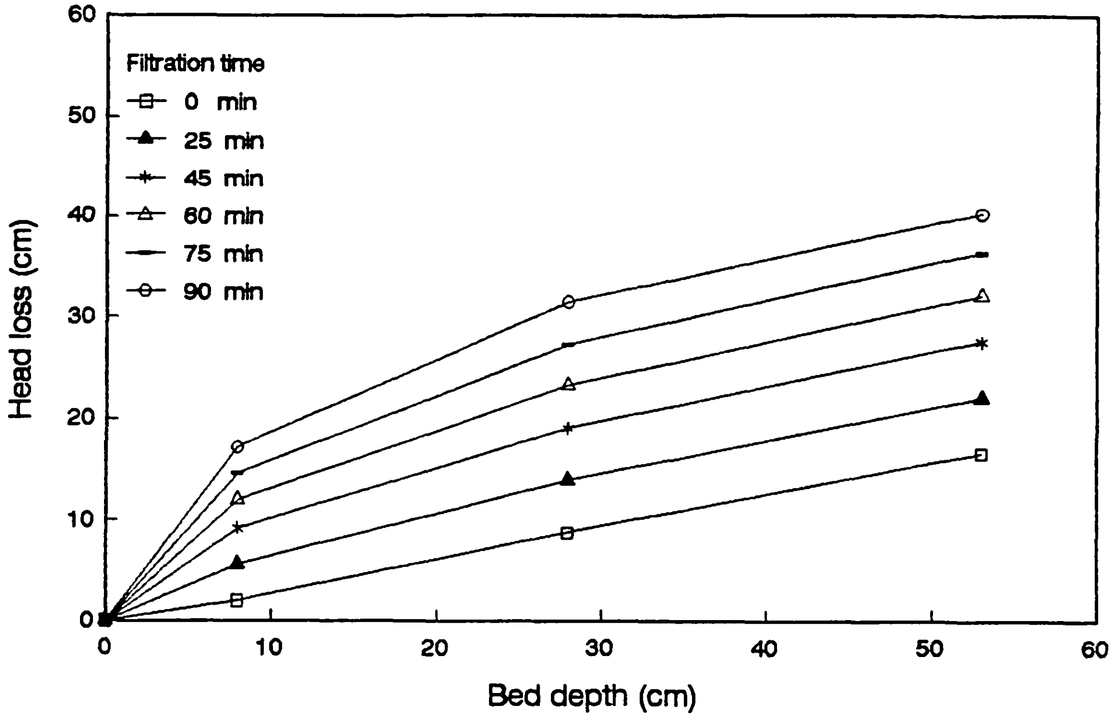
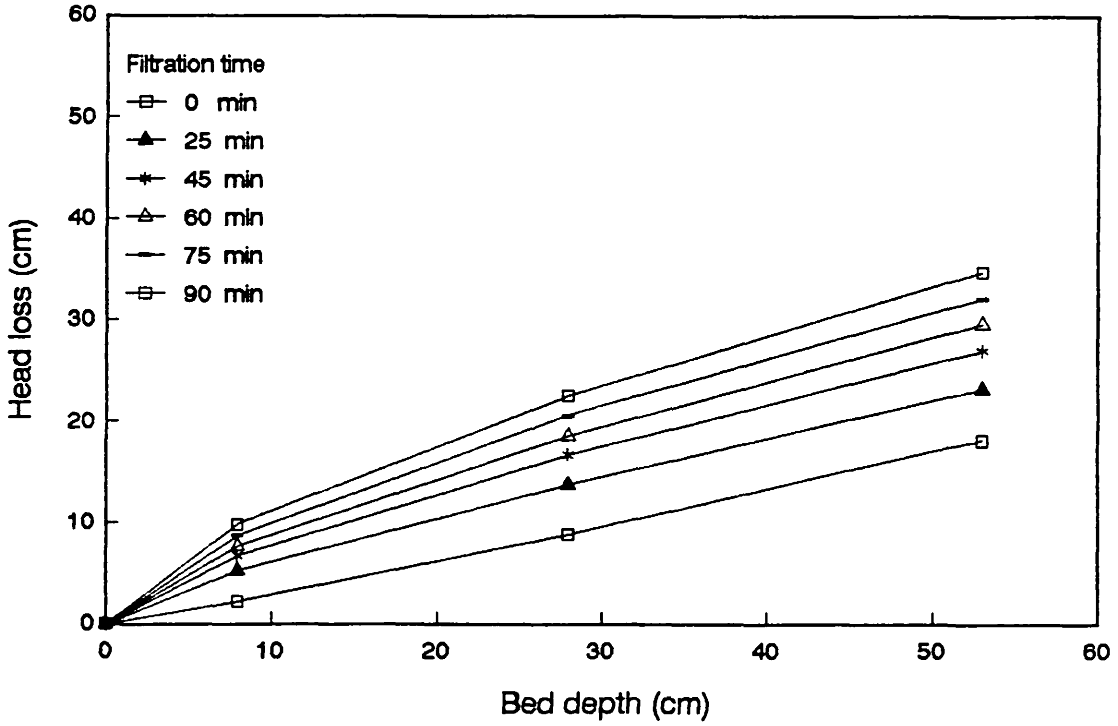


Figure 3.23: Filtration tests - High coloured water (5 Abs. units/m)



40 mg/l alum + 4 mg/l polymer



40 mg/l alum + 6 mg/l polymer

Figure 3.24: Head loss across the filter bed at various filtration times (typical example)

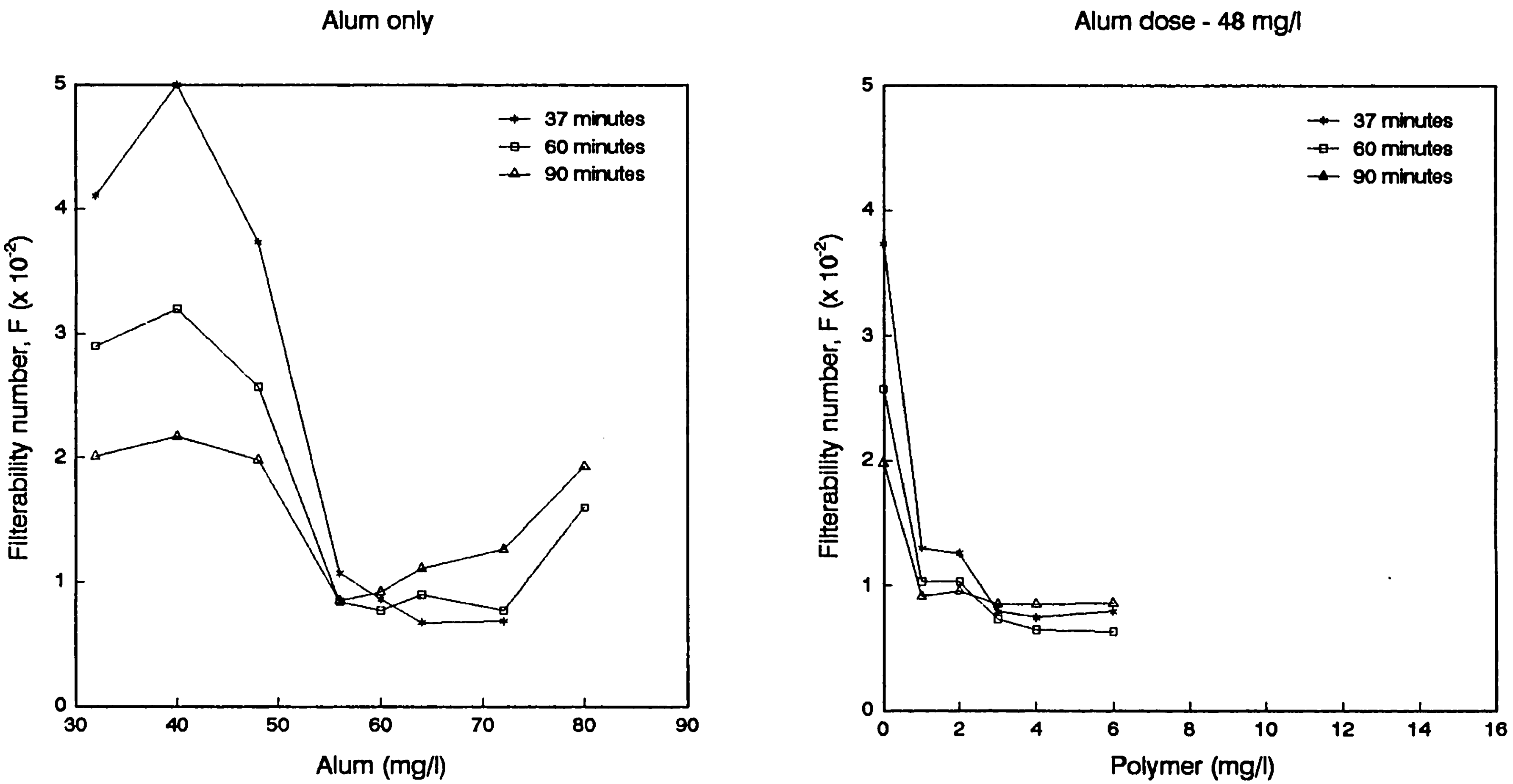


Figure 3.25: Filtration tests - Filterability number at various times
High coloured water

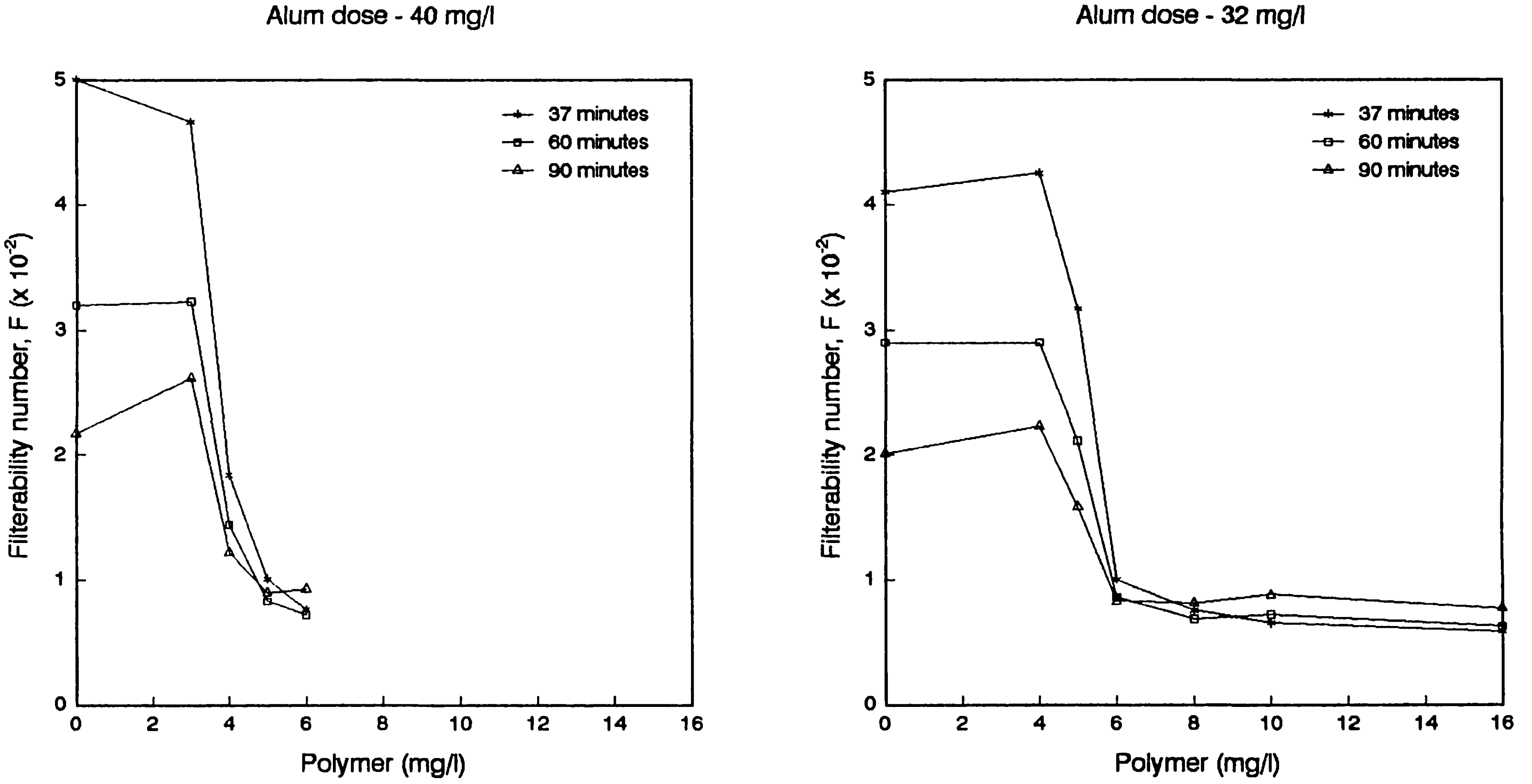


Figure 3.26: Filtration tests - Filterability number at various times

High coloured water

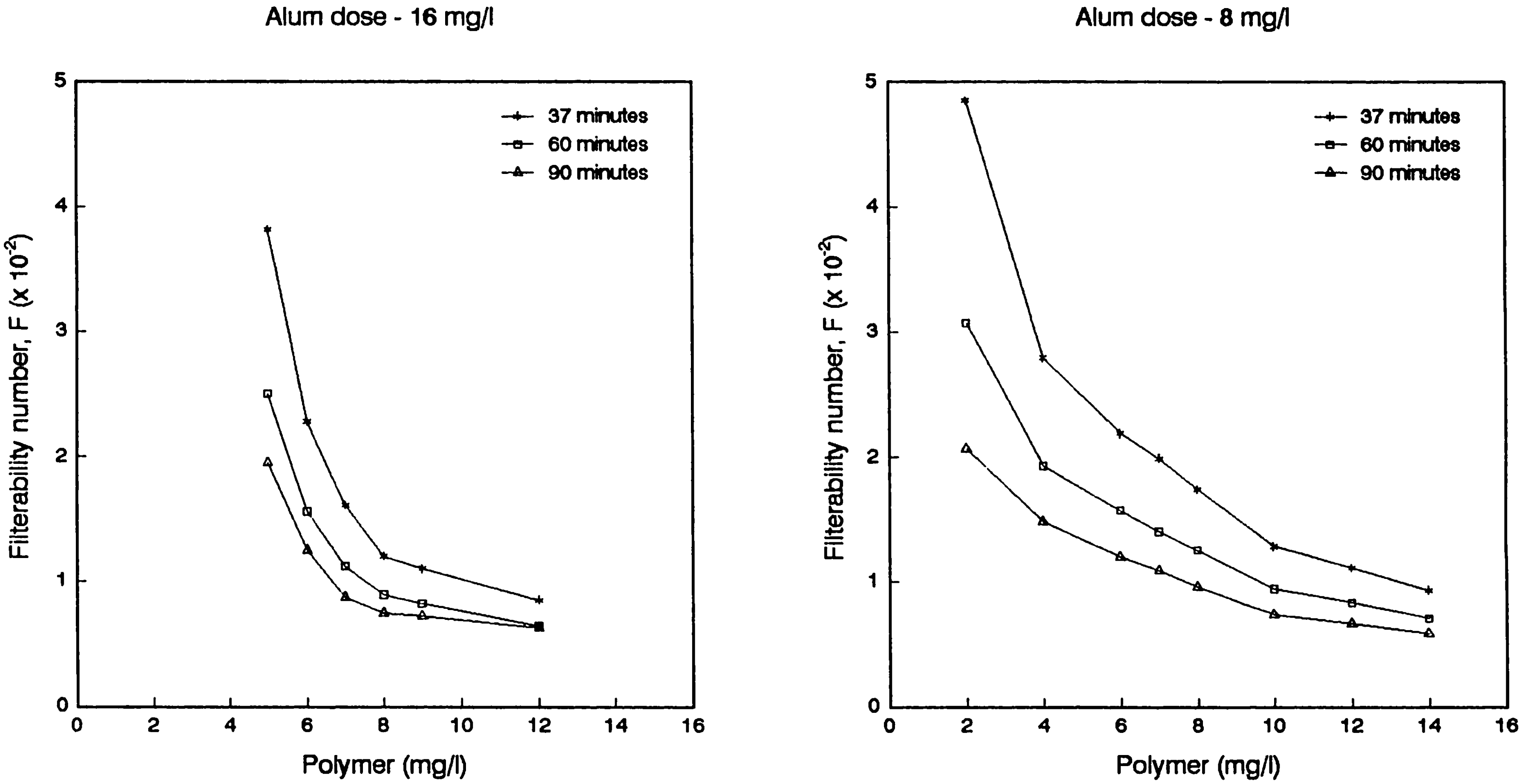


Figure 3.27: Filtration tests - Filterability number at various times

High coloured water

Optimal alum-polymer combinations

The shape of the filterability number curves determined for the moderate coloured water (figures 3.16) indicates that for each constant alum dose there is a specific polymer dose for which the filtration performance is maximum (minimum *F* value). However, it can also be observed from those curves that a near-maximum performance can generally be obtained at polymer doses considerably lower than that corresponding to the best performance.

In view of the need to minimize coagulant doses in practice, the optimum alum-polymer combination for a set of filtration tests is defined in this investigation as the combination that gives the 'practical-minimum' filterability number after 90 minutes of filtration. This practical-minimum *F* value corresponds, for a given alum concentration, to the minimum polymer dose for which there is no substantial further reduction in the filterability number value with the increase in polymer dose. Based on this criteria the optimum combinations were chosen. In the selection process the filtration tests using polymer and alum as sole coagulant were treated as a particular case of combination where the dose of the complementary coagulant was constant and equal to zero.

The locus lines of the optimal alum-polymer combinations selected for the moderate and high coloured waters are shown in figure 3.28. Although non-linear in nature, the locus lines can be approximated to a straight line of form $y = -ax+b$ that suggest that in practical terms the two coagulants act complementary. The similar shape of the locus curve for the moderate and high coloured water and their relative positions, suggest a linear relationship between colour concentration and dose of coagulants required to produce relatively similar filtration performance.

The values of the filterability number, filtrate quality (C/C_0*) and residual aluminium concentration at 90 minutes that correspond to the optimum alum-polymer combinations selected for the moderate coloured water (A to E) are shown in figure 3.29.

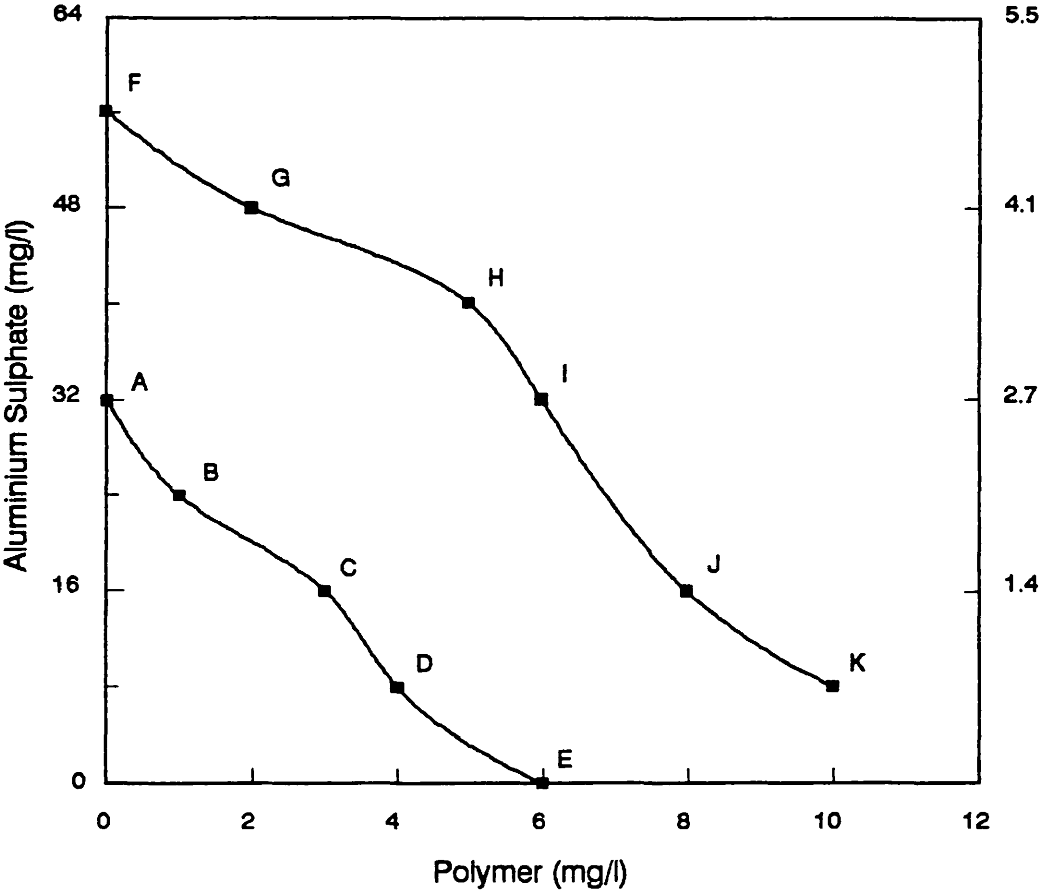


Figure 3.28: Locus of optimal alum-polymer dose combinations

Line A to E - Moderate coloured water (2.5 Abs. units/m)

Line F to K - High coloured water (5 Abs. units/m)

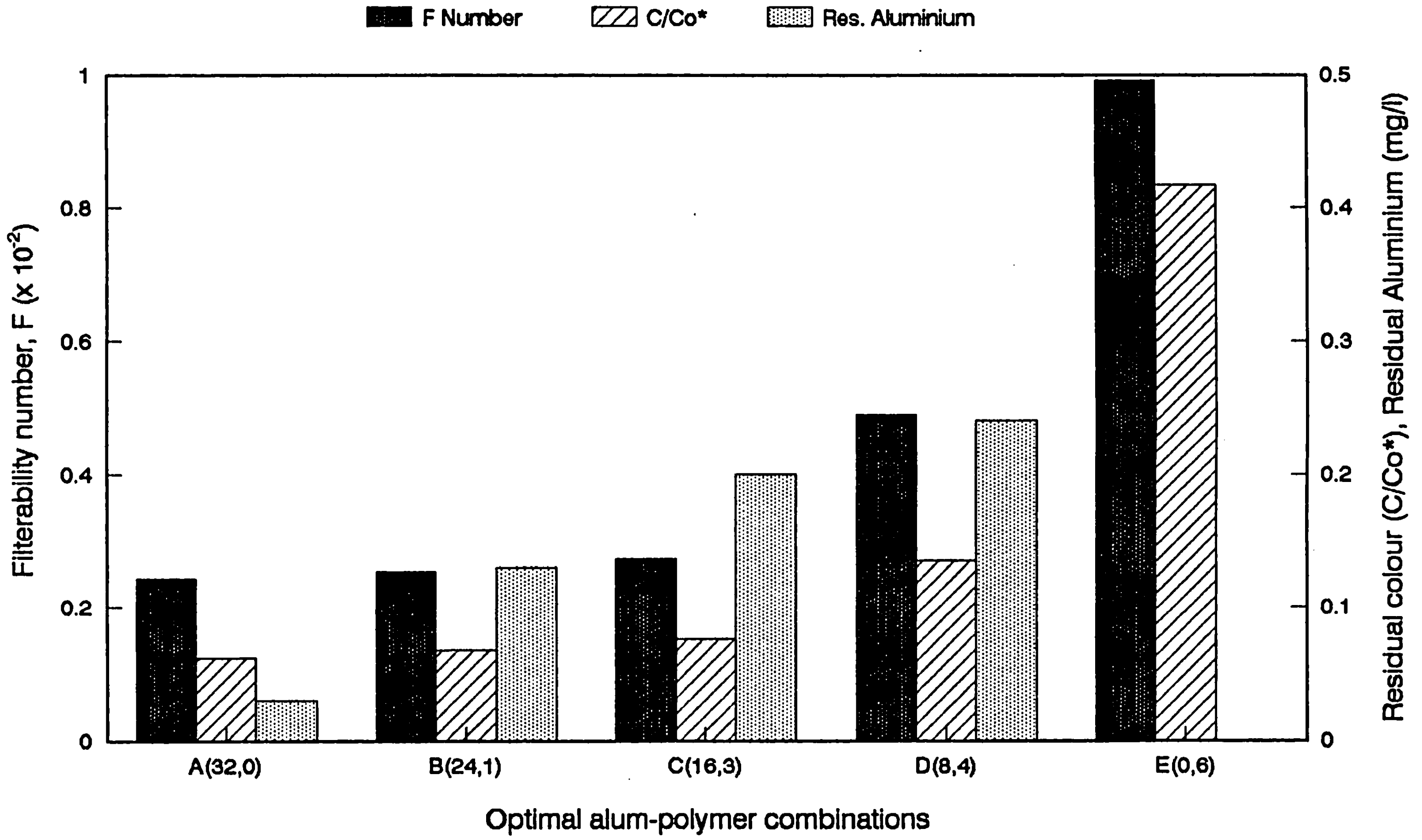


Figure 3.29: Variation of filterability number, residual colour and residual aluminium along the locus line (A to E) - Moderate coloured water

It can be seen from figure 3.29 that for the moderately coloured water the best filtration performance, based on the minimization of both *F* and residual aluminium, is achieved when aluminium was used alone and the worst (higher filterability number) when polymer was used alone. Also, the combination of alum and polymer tends to be more effective in removing colour when high alum doses are used. The use of lower alum doses than that corresponding to the optimum dose for alum as sole coagulant was not effective in promoting lower residual aluminium concentrations.

Figure 3.30 shows the values of filterability number, filtrate quality and residual aluminium concentration at 90 minutes corresponding to the optimum combinations for the highly coloured water (F to K). Whereas in the previous case (lower colour) a decrease in aluminium dosage tends to worsen the filtration performance resulting in an increase of the value of *F*, in this case the performance of the filter does not seem to vary significantly for the various optimum alum-polymer combinations. Moreover, in contrast with the trends observed for the moderately coloured water, the decrease in the dose of the aluminium sulphate component at the optimum alum-polymer combinations led to lower concentrations of residual aluminium in the filtered water.

The distinct variation of the filterability number values at 90 minutes observed for the two colour concentrations appears to be explained by the occurrence of the breakthrough within 90 minutes in most of the filtration tests performed with the higher coloured water. Whereas for the moderate colour the filterability number values were always calculated before the breakthrough, for the high coloured water the value of *F* was calculated sometimes before, sometimes after the quality breakthrough.

To improve matters, a comparison between residual colour (C/C_0*) and filterability number values obtained at 90 minutes and 37 minutes (time where no breakthrough occurs in any filtration experiment) for each of the optimum alum-polymer combinations is shown in figure 3.31.

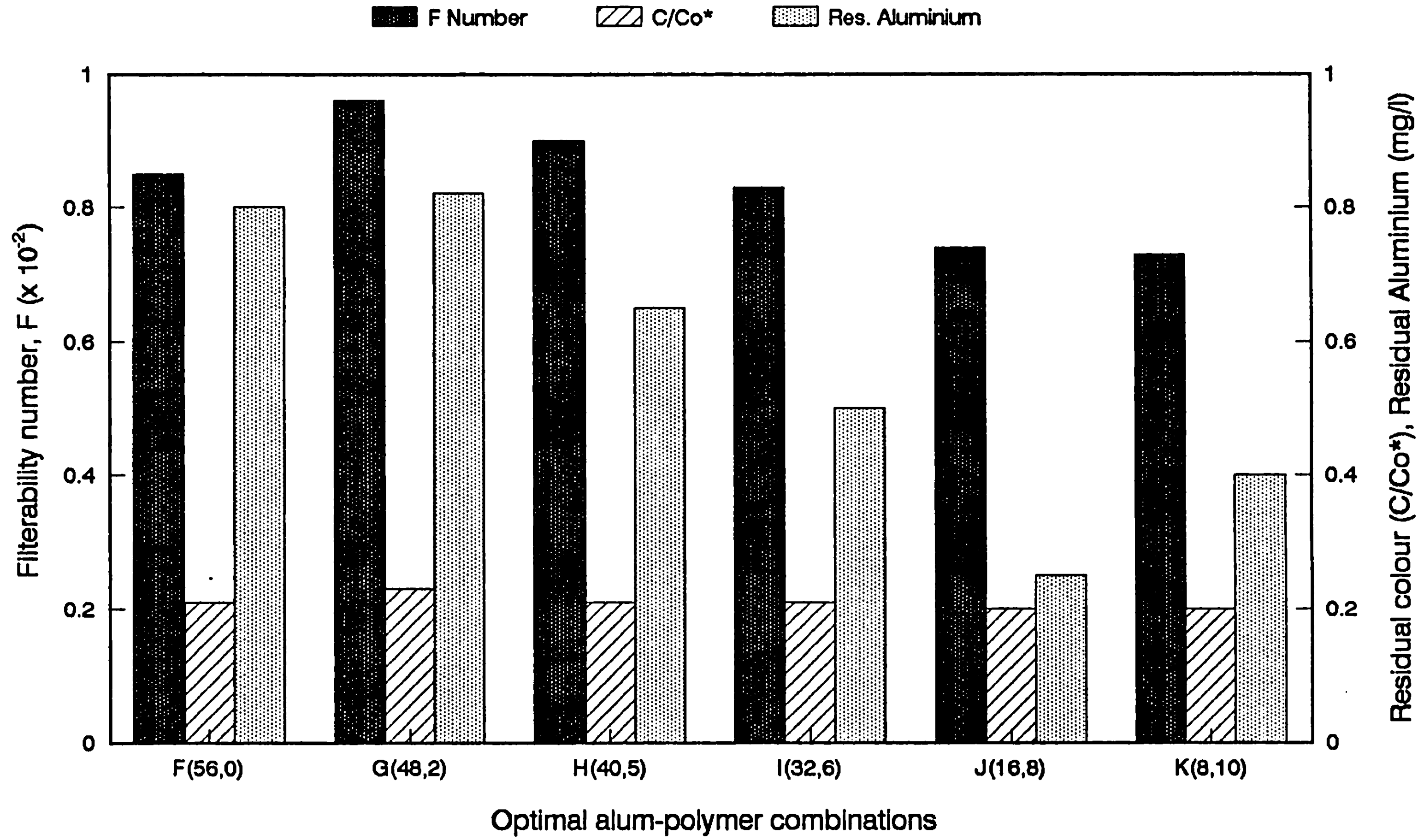


Figure 3.30: Variation of filterability number, residual colour and residual aluminium along the locus line (F to K) - High coloured water

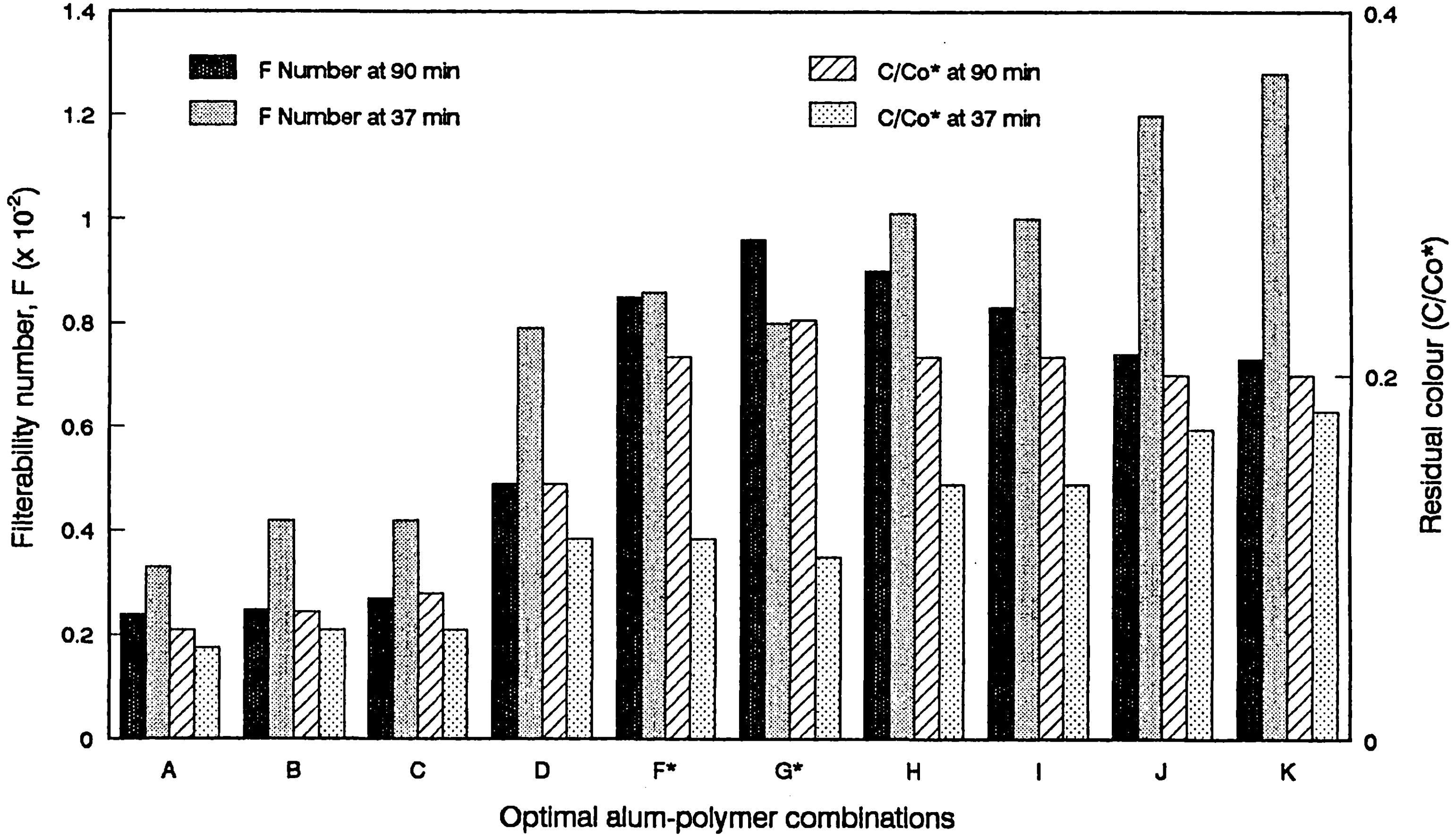


Figure 3.31: Comparison of filterability number and residual colour at different times

(* Optimum combinations do not coincide for F at 90 and 37 minutes)

It can be readily seen that for the moderate coloured water the behaviour of the filterability number is not affected by the filtration time used in calculation, while for the highly coloured water the filterability number values calculated at each time follow different trends. Moreover, when the pre-breakthrough condition is considered in all calculations (37 min of filtration), the filterability number values for the high colour concentration exhibit the same trend as for the lower colour concentration, i.e. the value of F increases (worsening of performance) with the decrease of the dose of alum in the alum-polymer combination. It is important to point out that the optimum combinations selected using F at 90 minutes and F at 37 minutes coincide, except for the case of high colour concentration when the alum dose in the combination was very high and when alum was used as sole coagulant.

It can also be observed from figure 3.31 that, whatever the filtration time taken, there is a direct relation between colour removal and filterability number, suggesting that the filterability number was less sensitive to head loss than to colour removal.

Similarly to the filterability number at 90 minutes, the concentration of residual aluminium at 90 minutes corresponding to the optimum combinations follow contrasting trends with the decrease of the alum concentration in the combination. Once again, this difference in behaviour is thought to be related to the occurrence of quality breakthrough prior to 90 minutes for the highly coloured water. However, experimental confirmation of this supposition was not possible owing to the fact that no composite sample of the filtered water was collected at 37 minutes of filtration (see sections 3.2.2.2 and 3.2.3).

In the case of the high coloured water most of the residual aluminium present in the filtrate is believed to come from the fraction of the flocculated material that was not retained in the filter bed, and therefore is mostly in precipitated form. This hypothesis is supported by the observation that, for each optimum combination, the proportion of aluminium residual to aluminium added was similar to the residual colour ratio (see figure 3.32). The only exception occurred when the lowest aluminium dose was used (8 mg/l of alum, 0.7 mg/l as aluminium).

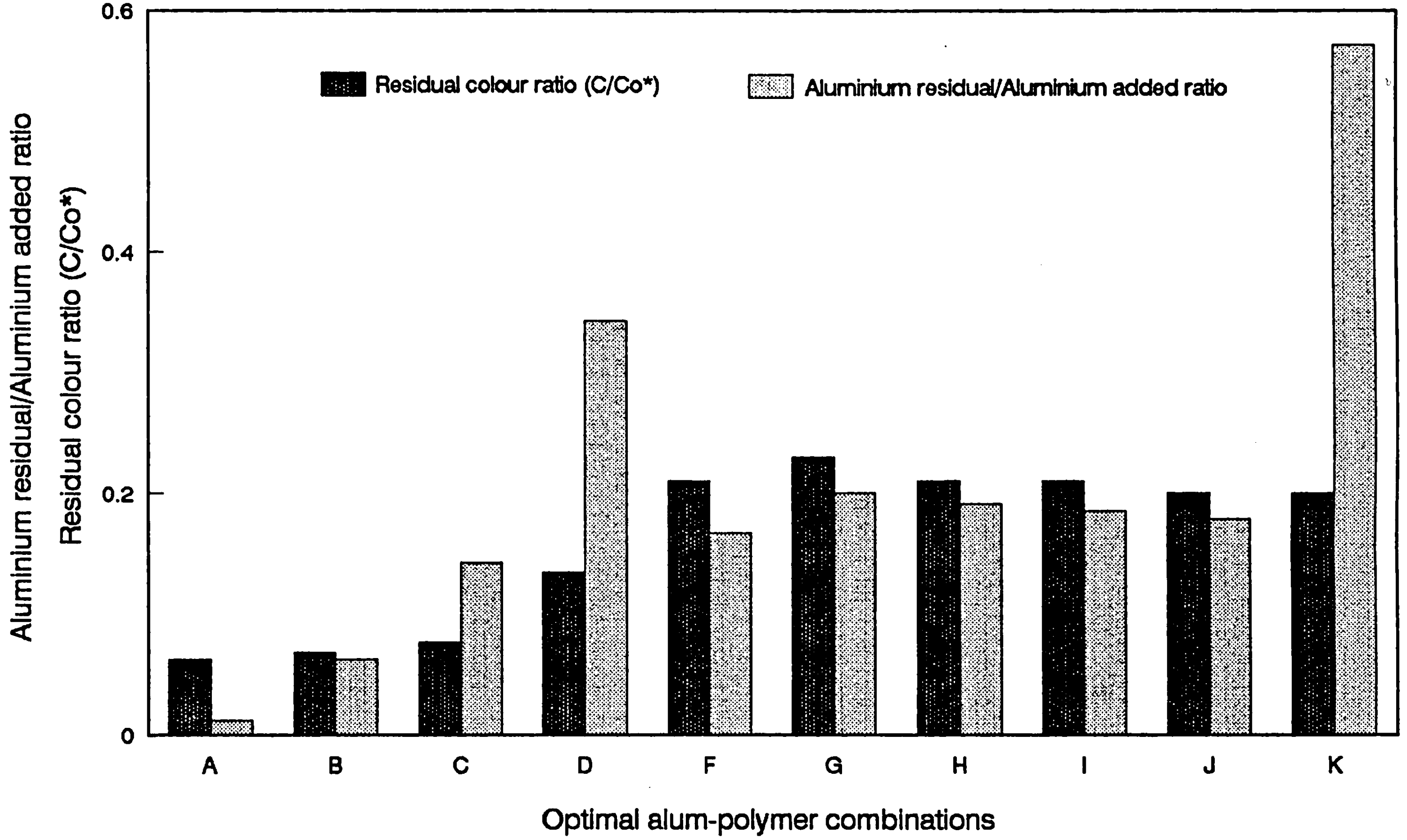


Figure 3.32: Residual colour and aluminium residual/aluminium added ratio at the optimal alum-polymer combinations

For the low coloured water it was observed that the filtration can effectively remove the flocculated material fed to the filter. It suggests that the cause of the residual aluminium in this case is probably related to the presence of free soluble aluminium or soluble aluminium-humic complexes in the filtrate instead of no-retained precipitated aluminium. Because the hydrolysis of aluminium is concentration dependent, the formation of a significant proportion of monomeric species of aluminium increases with a decrease of the alum dose. This explains the observed increase of the residual aluminium concentration with the decrease of alum dose. Monomeric species of aluminium can either be free and/or form stable complexes with the humic and thereby remain in solution.

4. FLOC CHARACTERIZATION

4.1 Introduction

It is known that the basic characteristics of the particle/floc (size, charge, strength etc.) have a strong influence on the effectiveness of the most common processes used in water treatment such as settling, flotation and filtration.

Particularly in filtration the particle characteristics can affect both transport and attachment mechanisms (Ives, 1970, 1982; O'Melia, 1985; Amirtharajah, 1988). Whereas the dominant transport mechanism is influenced by the particle size, the attachment mechanism is highly dependent of surface properties of both suspended particles and filter media.

In the present work two basic characteristics of the particles being filtered were studied: the floc size distribution and the floc charge. The objective of these measurements was to try to correlate such characteristics with the filter performance.

4.2 Experimental procedure

4.2.1 Floc size measurements

Two similar Malvern Particle Size Analyzers - Series 2600c (Malvern Instruments Ltd., Malvern) were used to perform most of the floc size distribution measurements. The two Analyzers differed only in the range of sizes covered, with one machine covering a maximum size range of 0.5 to 584 microns (3 different receiver lenses with ranges of 0.5 to 118, 1.9 to 188 and 5.8 to 584 microns) and the other covering a range from 11.6 to 1880 microns (3 receiver lenses with ranges of 11.6 to 1128, 15.5 to 1540 and 19.4 to 1880). In each case the lens covering the wider range of sizes was used.

A schematic diagram of the experimental set up used is shown in figure 4.1. It consists basically of the filtration apparatus described in

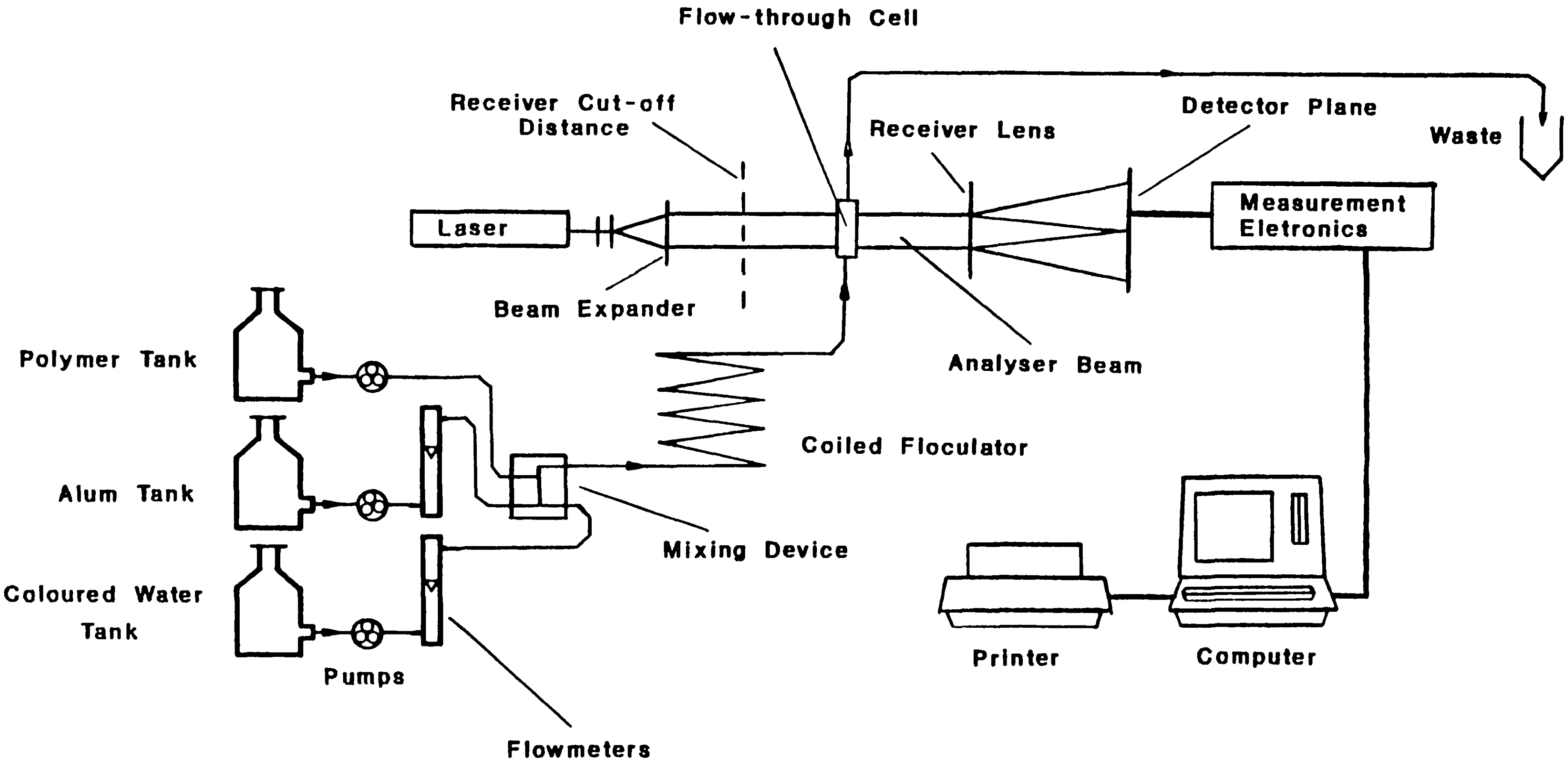


Figure 4.1: Floc size measurements schematic diagram

Alum-polymer combination experiments

section 3.2.2.1 without the filter itself and connected directly to the particle size measuring equipment. The Malvern particle size analyzer was connected 'in-line' to the coiled tube flocculator by means of a flow-through measuring cell. This arrangement has the advantage of monitoring the flocs as they would enter the filter, thereby causing the flocs much less disturbance than when samples are taken from the flow and transferred to another place to be measured.

The Analyzer instrument used operates on the principle of laser diffraction, a non-intrusive technique which does not require calibration. A light from a low power Helium-Neon laser source is used to form a collimated monochromatic beam of light. The particles when placed in this beam diffract the light which is then collected by a lens and brought to a focus on a special detector located in the focal plane of the lens. The detector, consisting of 31 concentric annular photosensitive rings, gathers the diffracted (scattered) light energy over a range of solid angles of scatter. The scattering angle is related to the diameter of the particle, with larger particles scattering light into smaller angles.

The detector provides an output signal proportional to the light energy measured over 31 separate solid angles of collection. The computer reads this signal and performs the time averaging by successively reading the detector over a set period of time and summing the data. The computer, using the software incorporated to the equipment, deduces the volume size distribution that gives rise to the observed scattering characteristics.

Preliminary tests with the instruments described above showed that the flocs (precipitate) formed when polymer was used as sole coagulant were very small with sizes below the detection level of the equipment. To measure these flocs (precipitate) another particle size analyzer (Autosizer II, Malvern Instruments, Malvern) capable of measuring particles with diameters between 3 and 3000 nanometres was used. The operational principle of this equipment is that of Photon Correlation Spectroscopy.

Photon correlation spectroscopy (PCS), also known as Quasi-Elastic Light Scattering (QELS) or Dynamic Light Scattering (DLS), is a new, fast, absolute (no calibration is needed) and non-destructive method for particle size determination in the sub-micron range. Using this technique the particle size is determined from the Brownian diffusion coefficient which in turn is calculated from the time constant of the auto-correlation function of the fluctuation in light scattered at 90 degrees (Leitzelement et al., 1987).

Figure 4.2 presents a schematic layout of the equipment used, with particular attention to the optical measurement unit (spectrometer). When a laser bean is passed through a dilute suspension of non-interacting particles, the light scattered from these particles will spread out into the space surrounding the sample and a small portion of this light will be received through the imaging optics of the detection system situated close to the sample at an angle of 90°. The detector senses the intensity of the radiation which is a measure of the instantaneous position of the particles.

Since the particles are moving under Brownian diffusion and the detector is sensitive to their positions, the intensity measurements fluctuate in time. Although the movement is essentially random it can be characterised by a diffusion time and this reflects itself in the period of fluctuation in intensity. In other words, a small particle undergoing a rapid Brownian motion will generate a rapidly fluctuating intensity in the scattered signal. Similarly, large particles diffusing more slowly will result in a slower evolution of the intensity as a function of time.

The light intensity fluctuation can be computed by the so-called 'correlator' (a simplified computer dedicated to this specific task) to generate an auto-correlation function. In the equipment used the correlator operates by sampling the signal at a number of discrete time intervals known as sample times and the light intensity during each of these sample times is measured as a certain number of photons being detected. This correlator works at four simultaneous sample times which

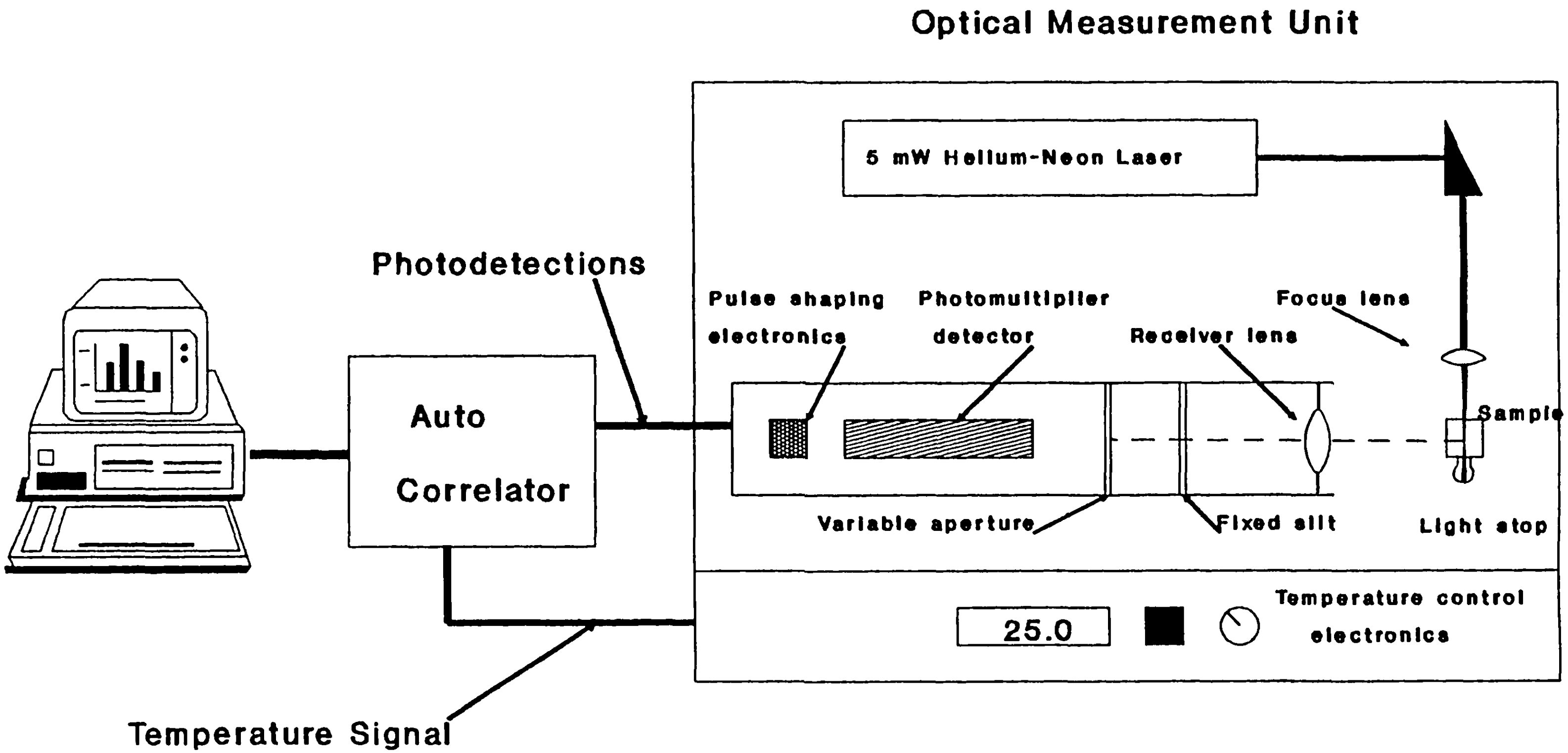


Figure 4.2 : Schematic layout of Autosizer II

the manufacturer claims to be more effective in dealing with wide ranges of particle sizes. The computed auto-correlation function $C(\tau)$ that is function of the light intensity at time t, $I(t)$, and at an earlier time $t-\tau$, $I(t-\tau)$, presents an exponential decay shape as shown in figure 4.3.

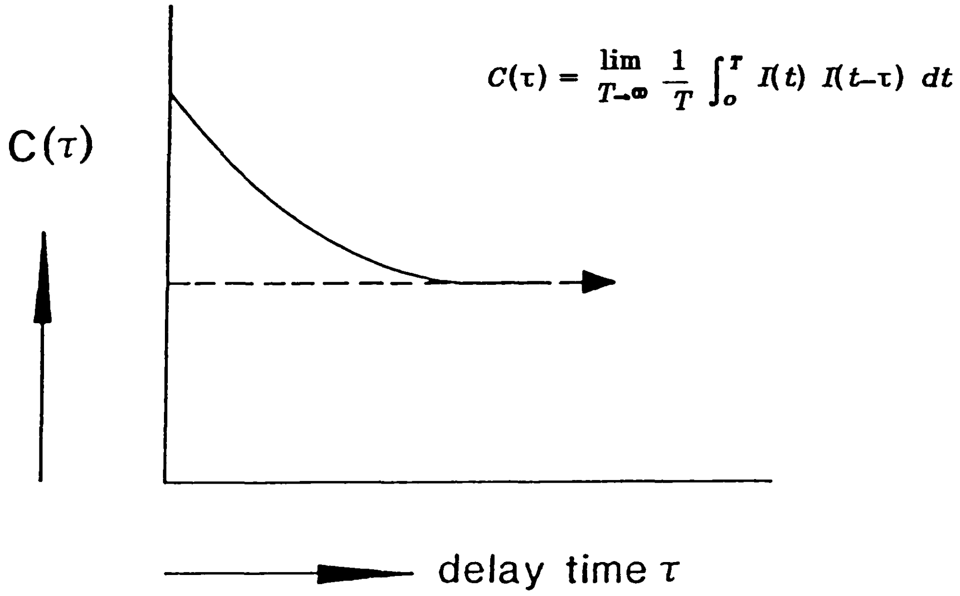


Figure 4.3: PCS auto-correlation function of scattered light intensity (after Scarlett et al., 1988)

For particles of uniform size the resultant auto-correlation, $C(\tau)$, after subtraction of the base line is:

$$C(\tau) = A \exp[-2Dq^2\tau] \tag{5}$$

with

$$D = \frac{kT_a}{6\pi\eta R_H} \tag{6}$$

and

$$q = \frac{4\pi m}{\Lambda}\sin(\theta/2) \qquad (7)$$

Where τ is the delay time;

D is the translational diffusion coefficient in Stokes-Einstein equation;

q is the length of the wave vector which is constant for an specific source and a fixed angle θ;

η is the solvent viscosity;

m is the refractive index of the solvent;

T_a is the absolute temperature;

k is Boltzmann's constant;

Λ is the wavelength of the source (He-Ne laser 632.8 nm);

R_H is the hydrodynamic radius of the particle.

However, for polydispersed samples the interpretation of the data (light intensity fluctuation) is much more difficult. Stanley-Wood (1987) explains: "Because single particles are not counted the size distribution (in a polydispersed system) must be obtained by the deconvolution of the sum of all single exponential contributing to the evaluated auto-correlation function. Thus with a highly polydispersed size distribution the DLS technique does not perform well as all differently sized particles in the moving particulate systems are measured at the same time. There is no separation of particles in various sized classes and therefore there is no physical means to quantify individually particles into separate classes. The proportion of each class or size of particles has to be separated and classified by mathematical analysis of the auto-correlation function.".

For polydispersed mixtures of different sizes with diffusivity D_i, Stanley-Wood (1985) defines the auto-correlation function as:

$$C(\tau) = A \left[\sum_{i=1}^{N} f_i \exp[-D_i q^2 \tau] \right] \qquad (8)$$

The correlation function now combines the weighted sum f_i of each decaying exponential corresponding to a specific particle radius of the N number of different sizes. Numerous mathematical methods have been used to obtain the weight coefficient and to discriminate between classes of particles from the correlation function.

In the equipment used the cumulant analysis method is applied to transform the auto-correlation function to particle size distribution for unimodal and narrow spreads in size systems. To deal with broad distributions the instrument contains a distribution analysis algorithm which tries to fit an essentially model free distribution to give the best fit to the correlation function that has been measured. This is done by storing a model of the correlation functions that would be expected from a wide range of particle sizes and finding the best combination of these correlation functions to fit the measured data. However, very little detail of the algorithms used is available and the software associated with is closely guarded.

The polymer floc measurements, due to characteristics of the equipment which only accept 10 mm ordinary spectrophotometer cells, were not done in the in-line mode as the previous floc size determinations. Moreover, due to the short time period of availability of the equipment (on loan from the SERC equipment loan pool), it was chosen to perform these measurements based on coagulation experiments using the jar test apparatus, instead of using the coiled flocculator which was more time consuming. The coagulation tests at the various polymer doses were performed according to the procedure described in section 3.2.1 and at the end of the slow mixing period an aliquot of the coagulated water was carefully transferred to the measurement cell and put into the instrument. A short standing time was then allowed in order to stabilize the temperature of the sample to a set value, 25°C, after which the measurement was performed following the procedure described in the equipment's manual.

In order to perform measurements of size distribution with the Autosizer II the only input data needed about the sample to be analyzed were the temperature, viscosity and refractive index of the medium, which was water in this case.

4.2.2 Floc charge

The equipment used to determine the electrophoretic mobility/Zeta potential of the flocs was a Rank Bros. Electrophoresis Apparatus (Rank Bros., Cambridge).

The electrophoretic mobility in this equipment is determined by a microscopic technique that views the motion of particles in a small horizontal cell subjected to an electrical potential (see figure 4.4). The velocity of a particle moving within the cell, the electrophoretic velocity, V_e (µm/s), is measured by timing its passage between graticule lines of known distance on an ocular scale and from this value the electrophoretic mobility, U (µm.s^{-1}/V.cm^{-1}), can then be calculated using the following equation (Faust and Aly, 1983):

$$U = \frac{V_e}{(E/L)} \tag{9}$$

where E is the applied electrical potential (in Volts) and L the distance (cm) over which the potential is applied. The electrical potential is controlled by the operator and in the equipment used could be varied from 0 to 100 volts. The distance L, on the other hand, is characteristic of each cell.

The zeta potential, ζ (mV), may be related to the electrophoretic mobility according to the expression (10) below, where ϵ and η are respectively the dielectric constant and viscosity of the medium. The value of K depends on the particle diameter and the thickness of the double layer of ions. For relatively large particles (Helmholtz model) K assumes the value of 4π (Degremont, 1979).

$$\zeta = \frac{K\eta}{\epsilon} U \tag{10}$$

For $K = 4\pi$ and water at 25° C equation (6) becomes:

$$\zeta = 13\,U \tag{11}$$

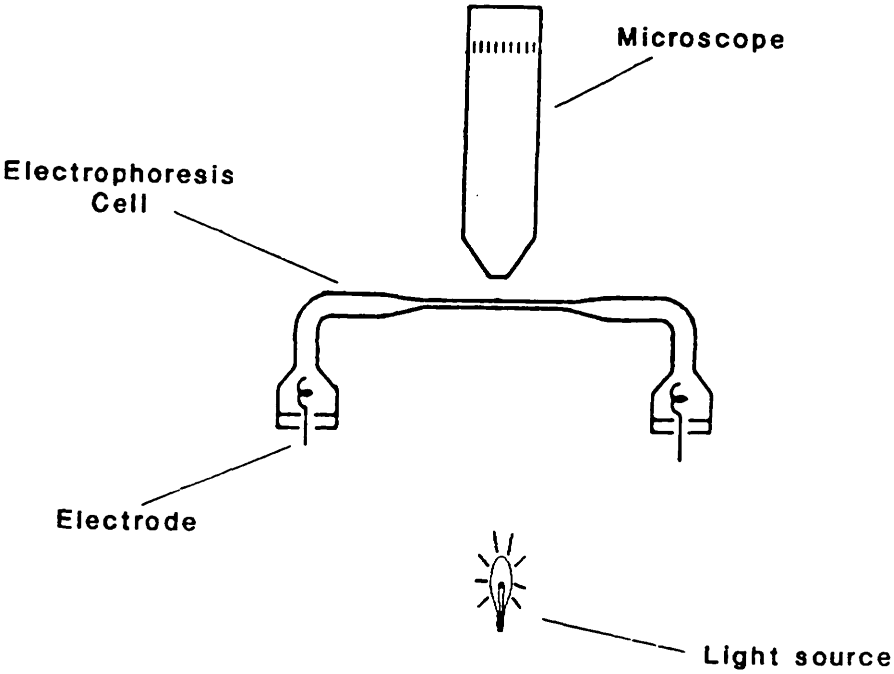


Figure 4.4: Schematic diagram of the electrophoresis apparatus

To perform the experiments the flocs were generated using the coiled tubing flocculator at the same coagulation conditions tested during the filtration experiments. The flocculated samples were taken direct from the end of the flocculator to the cell via a connecting piece of tubing.

The electrophoretic velocity determinations were carried out according to the procedure described in the equipment's manual. Each coagulation condition studied was tested at least two times on different occasions and in each experiment various samples of flocculated water were taken and a large number of determinations were made at both stationary levels.

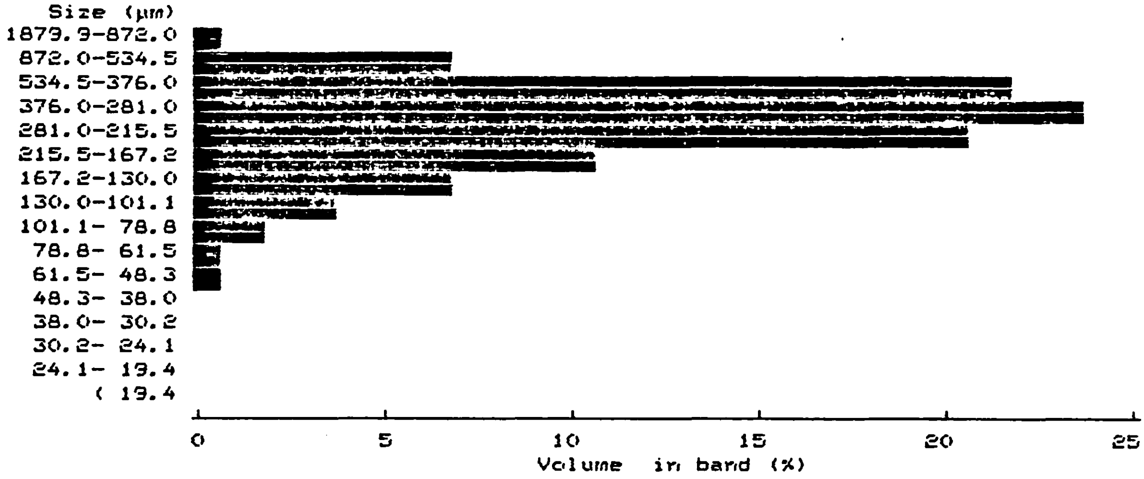
4.3 Results

4.3.1 Floc size measurements

All alum-polymer combinations tested during the filtration experiments with the moderate coloured water were repeated and had their floc size distribution measured. Measurements were made at two different flocculation times, 5 minutes and 14 minutes, with the other variables involved being kept constant.

Attempts were made to measure the flocs formed during flocculation of the high coloured water, but in most of the experiments the flocs were too large, with sizes out of the detection range of the equipments available.

A typical print-out of the floc size distribution measurements made using the laser diffraction instrument is shown in figure 4.5. The volume frequency of the distribution over 15 size bands is presented together with a summary of distribution parameters (d10, d50, d90, span, mean diameters, etc.). Figures 4.6 to 4.9 present the results of the mean floc diameter at 5 and 14 minutes as a function of polymer dose for each constant alum dose values. The mean floc diameter values plotted are the arithmetic mean diameter based on the volume distribution, the so called $d(4,3)$, which is defined by the following equation:



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Malvern Instruments  MASTER Particle Sizer M3.1 Date 14-10-88 Time 13-26
--------------------------------------------------------------------------
   Size                  |     Size band                | Result source=Sample
  microns     % under    |      microns            %    | Record No.    =   0
--------------------------------------------------------| Focal length =1000 mm.
   1879.9       100.0    |                              | Experiment type pil
    872.0        99.4    |   1879.9    872.0     0.6    | Volume  distribution
    534.5        92.2    |    872.0    534.5     7.3    | Beam length   =   2.0 mm.
    376.0        70.3    |    534.5    376.0    21.9    | Obscuration  =0.0469
    281.0        46.7    |    376.0    281.0    23.6    | Volume Conc.  = 0.1886 %
    215.5        26.1    |    281.0    215.5    20.6    | Log. Diff.    =2.75
    167.2        15.2    |    215.5    167.2    10.9    | Model indp
    130.0         8.3    |    167.2    130.0     6.9    |
    101.1         4.3    |    130.0    101.1     4.0    | D(v,0.5)    = 292.3 µm
     78.8         2.4    |    101.1     78.8     1.9    | D(v,0.9)    = 509.5 µm
     61.5         1.4    |     78.8     61.5     1.1    | D(v,0.1)    = 139.5 µm
     48.3         0.7    |     61.5     48.3     0.6    | D(4,3)      = 319.0 µm
     38.0         0.4    |     48.3     38.0     0.3    | D(3,2)      = 230.1 µm
     30.2         0.2    |     38.0     30.2     0.2    | Span        = 1.3
     24.1         0.1    |     30.2     24.1     0.1    | Spec. surf. area
     19.4         0.0    |     24.1     19.4     0.1    |     0.01 sq.m./cc.
--------------------------------------------------------------------------
Sample details:-Colour concentration 2.5 Abs units/m
Alum dose - 32 mg/l
No polymer addition
```

Figure 4.5: Floc size distribution print-out

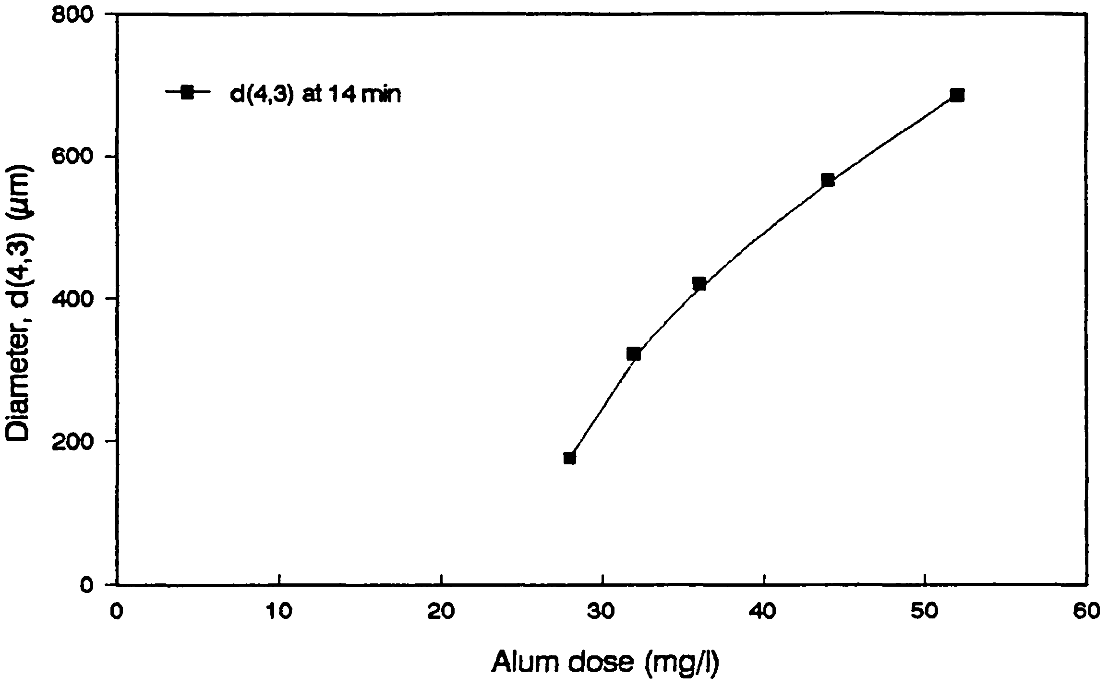


Figure 4.6: Mean floc diameter - Moderate coloured water
No polymer added

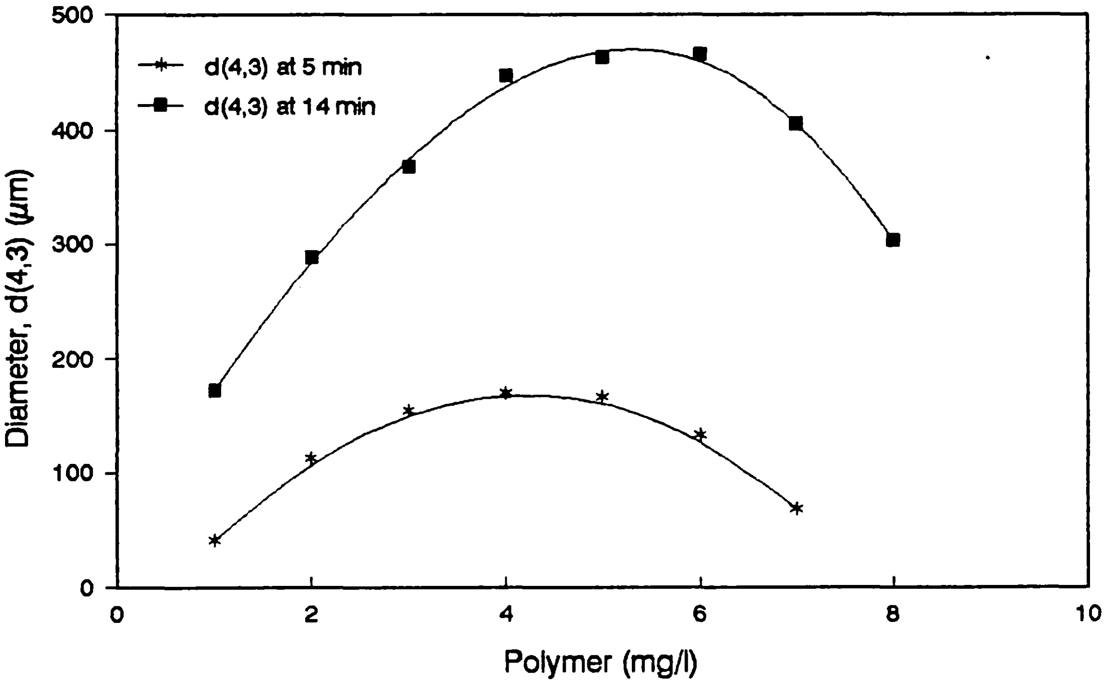


Figure 4.7: Mean floc diameter - Moderate coloured water
24 mg/l of alum

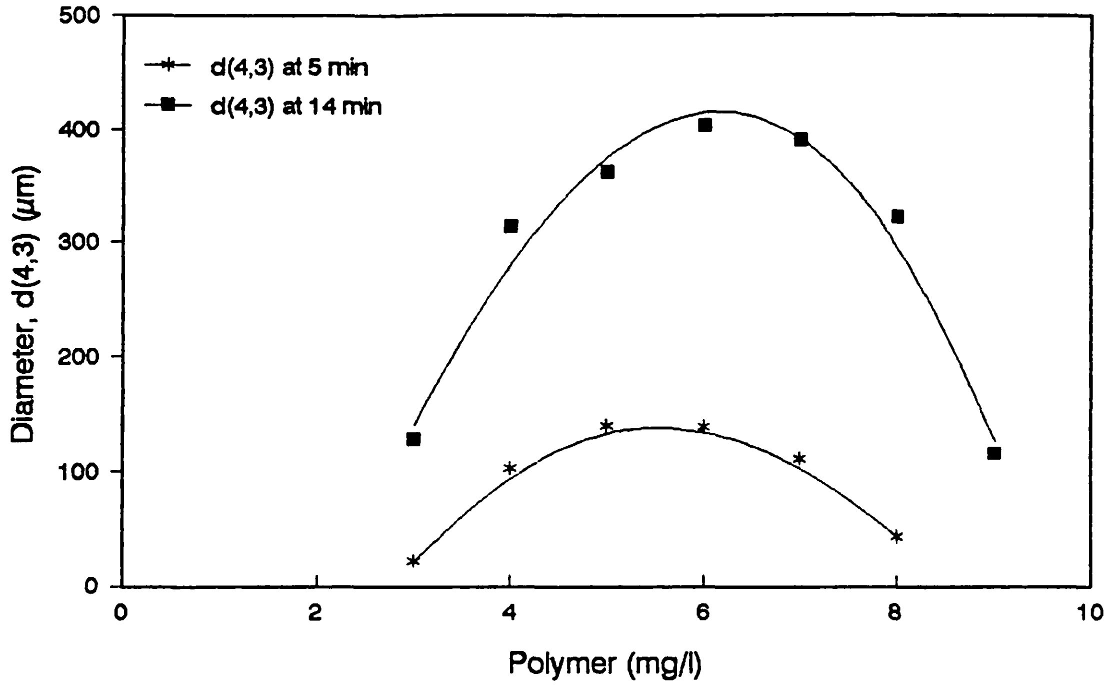


Figure 4.8: Mean floc diameter - Moderate coloured water

16 mg/l of alum

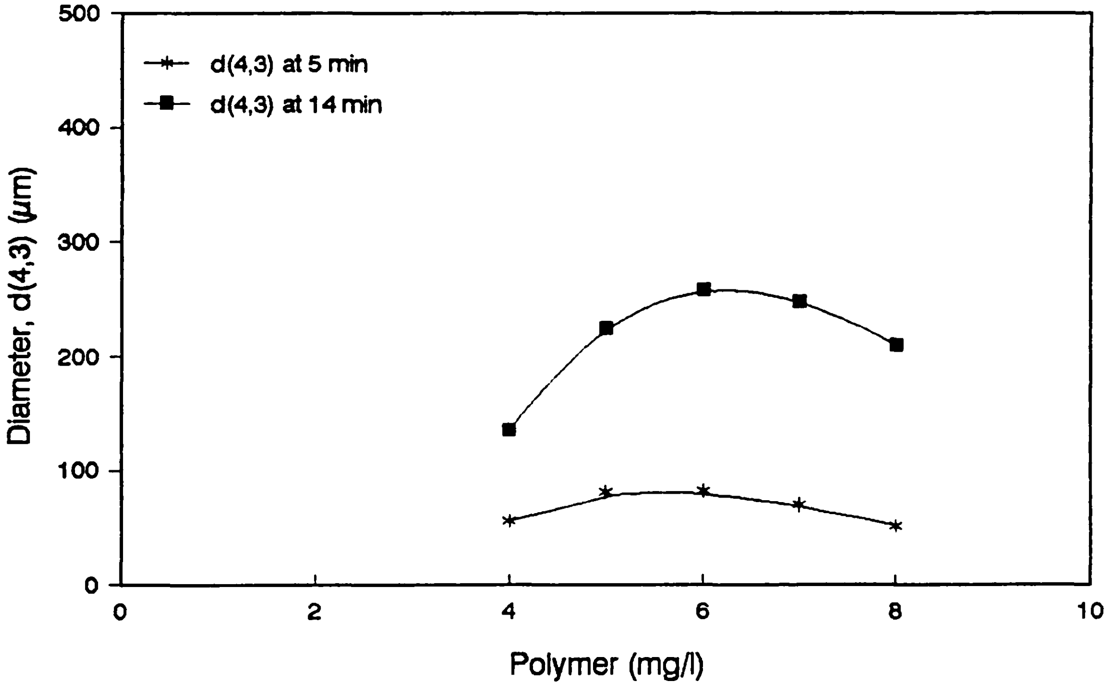


Figure 4.9: Mean floc diameter - Moderate coloured water

8 mg/l of alum

$$d(4,3) = \left[\frac{\int_{d_o}^{d_n} d^4 n(d)\, dd}{\int_{d_o}^{d_n} d^3 n(d)\, dd} \right] \tag{12}$$

Where $n(d)$, the number distribution, can be represented as function of the volume distribution $V(d)$:

$$n(d) = \frac{V(d)}{\frac{1}{6}\pi d^3} \tag{13}$$

By substituting equation (9) into equation (8) the $d(4,3)$ becomes a function of the volume distribution.

$$d(4,3) = \left[\frac{\int_{d_o}^{d_n} d\ V(d)\, dd}{\int_{d_o}^{d_n} V(d)\, dd} \right] \tag{14}$$

A mean diameter based on the volume distribution was basically chosen because, for design reasons, the instrument measurements are based on the volume of the particles present and all other outputs offered (number distribution, surface distribution etc) are numerical transformations of the basic output form, assuming spherical particles. Moreover, the volume size distribution emphasizes the degree of flocculation achieved with the different polymer doses whereas the number distribution, for instance, would probably mask such differences due to the larger number of small particles.

From the results some observations can be made:

(i) There is a considerable development in floc size between 5 and 14 minutes of flocculation, but the rate of growth depends on the polymer dose added. The polymer dose corresponding to largest mean floc size tends shifts to higher values with the increase in flocculation time;

(ii) The higher the alum dose component in the coagulant combination. the greater is the growth of the flocs;

(iii) The existence of a maximum floc size at each constant alum dose, when alum is used in combination with polymer, indicates that at polymer doses higher than that corresponding to the maximum mean diameter particle restabilization is taking place as a result of polymer overdose. When alum is used as sole coagulant a continuous increase in floc size is observed.

Figures 4.10 and 4.11 show the floc size results obtained for the coagulation experiments (jar test) using polymer as sole coagulants. The size distribution determination were performed over a period of time of 150 seconds, automatically divided by the equipment in ten shorter sub-runs adding up to the total time set. This operation mode enables the instrument to filter doubtful data affected by the presence of fluctuating components (e.g. dust crossing or particle motion due to environment turbulence) including in the final mathematical analysis only the good quality and consistent measurements (sub-runs) of the set. The quality of the data measured can be assessed using the '% in range' and the 'signal/noise ratio' figures determined at each measurement. While the vast majority of the experiments were characterized by very good 'in range' figures, relatively high noise values, but still in the acceptable range, were observed in the moderate coloured water determination. These high values were due to the use of a larger aperture on the photomultiplier detector.

For each flocculated water sample, the measured data was treated using both unimodal and model free analysis provided by the software related to the Autosizer. In the majority of the coagulation tests with both waters, moderate and high colour, the unimodal analysis presented a better fit of the calculated model to the correlation function measured. Therefore, the distribution mean diameter (*d*) and the *Z* average diameter values plotted in figures 4.10a and 4.11a are those obtained using the unimodal analysis.

The *Z* average diameter is the mean particle size based on the intensity (of light scattering) distribution and therefore does not take into account the different scattering ability of differently sized particles. It is proportional to the average diffusion coefficient calculated from the auto correlation function. The distribution mean diameter (*d*) is the arithmetic mean of the volume size distribution, which is itself the result of a correction in the intensity distribution taking in account the relationship between scattering ability and particle size assuming that the particles are spheres.

As can be seen both mean (*d*) and *Z* average diameter values follow a similar pattern. The variation in floc size with the increase in polymer dose is, in both cases, characterized by the presence of a maxima peak at relatively low polymer doses and a second region of increasing floc size at higher polymer doses. These results, due to their unusual pattern, were qualitatively checked by means of a simple filtration test. In this test samples of the coagulated water used in the size measurements were separately filtered through two different pore size filter paper (0.45 and 1.2 μm) and the quality of the filtered samples were then determined. The filtration results for each coloured water are presented in figures 4.10b and 4.11b.

As can be seen in figures 4.10 and 4.11, the filtrate quality results support the floc size results obtained. Moreover, the differences observed between the removal efficiency achieved by each filter paper emphasize the accuracy of the size measurements. The agreement between the variation in the filtrate quality and floc size is particularly clear for the high coloured water. In the regions of accentuated floc size increase (6 to 8 and 22 to 32 mg/l of polymer) an improvement in the quality of both filtered waters is observed, whereas

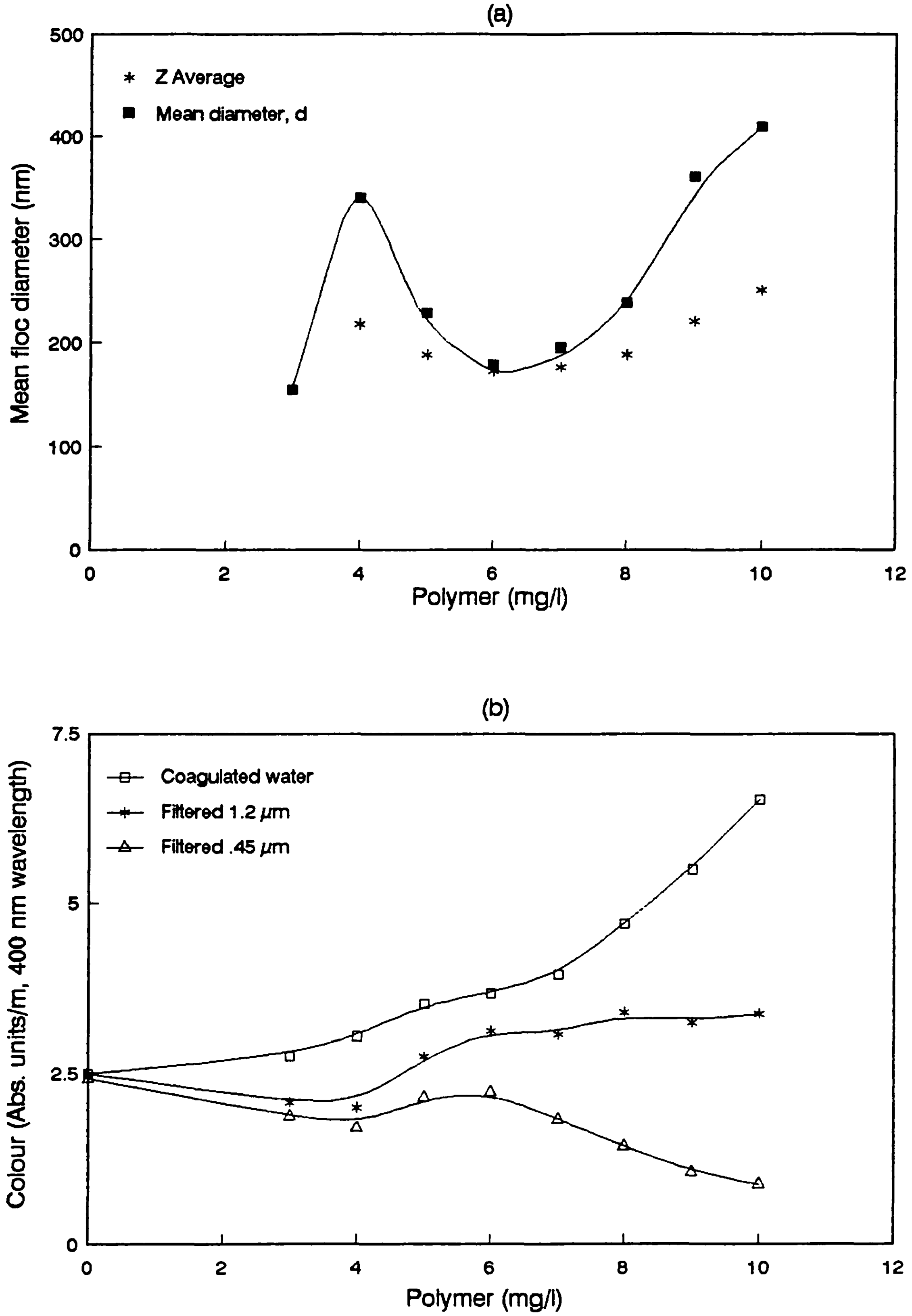


Figure 4.10: Variation of (a) floc diameter and (b) water quality with polymer dose - Jar test with moderate coloured water

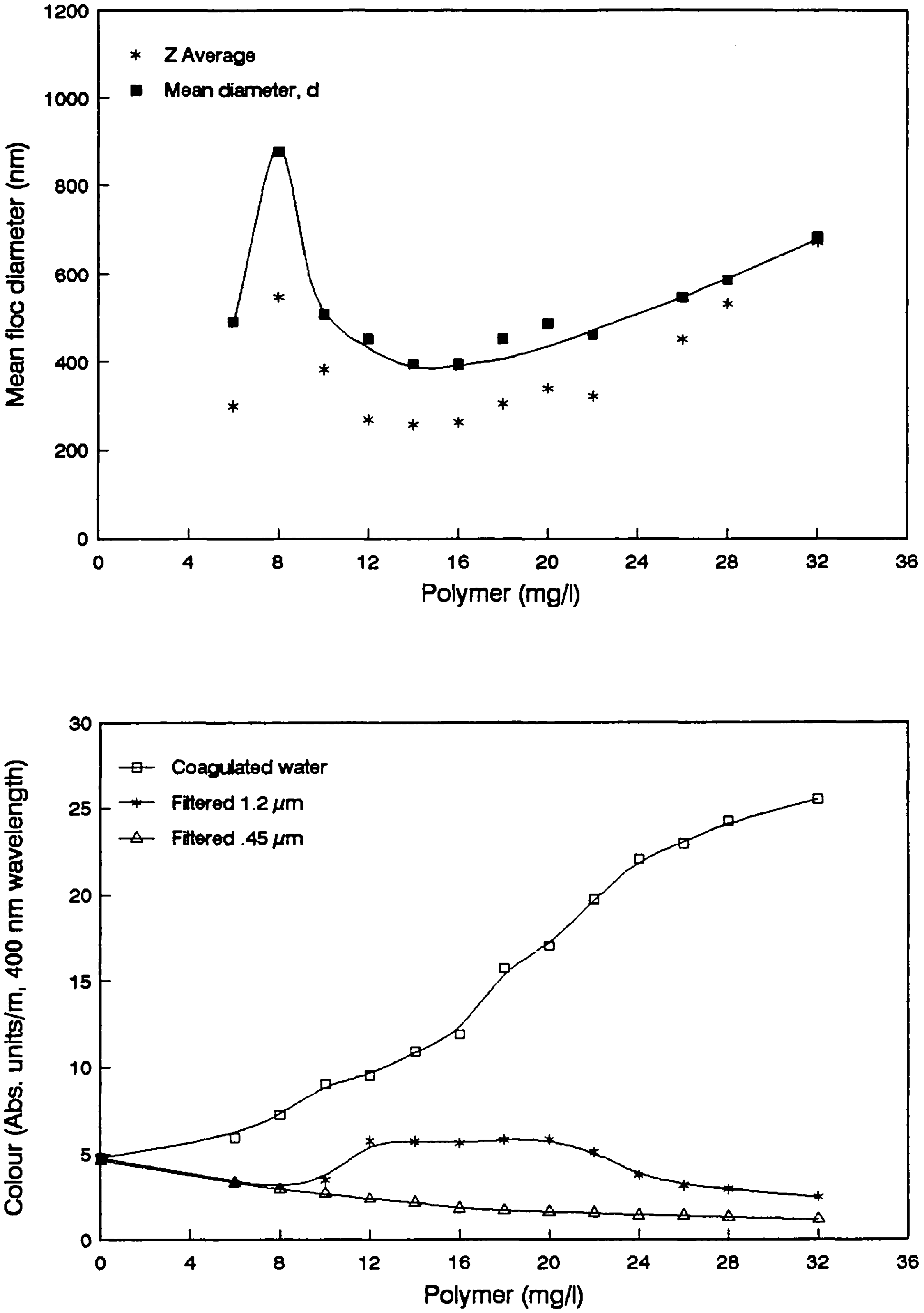


Figure 4.11: Variation of (a) floc diameter and (b) water quality with polymer dose - Jar test with high coloured water

in the mid-interval (smaller flocs) deterioration of the quality is observed but only for the 1.2 µm filtered water. The successful removal by the 0.45 µm filter in this latter region is consistent with the observed mean floc diameter values around 400 to 500 nm. The continuous improvement of the 0.45 µm filtered water over the whole range of doses studied suggests the formation of an increasing amount of flocs with diameters bigger than 0.45 microns.

4.3.2 Floc charge

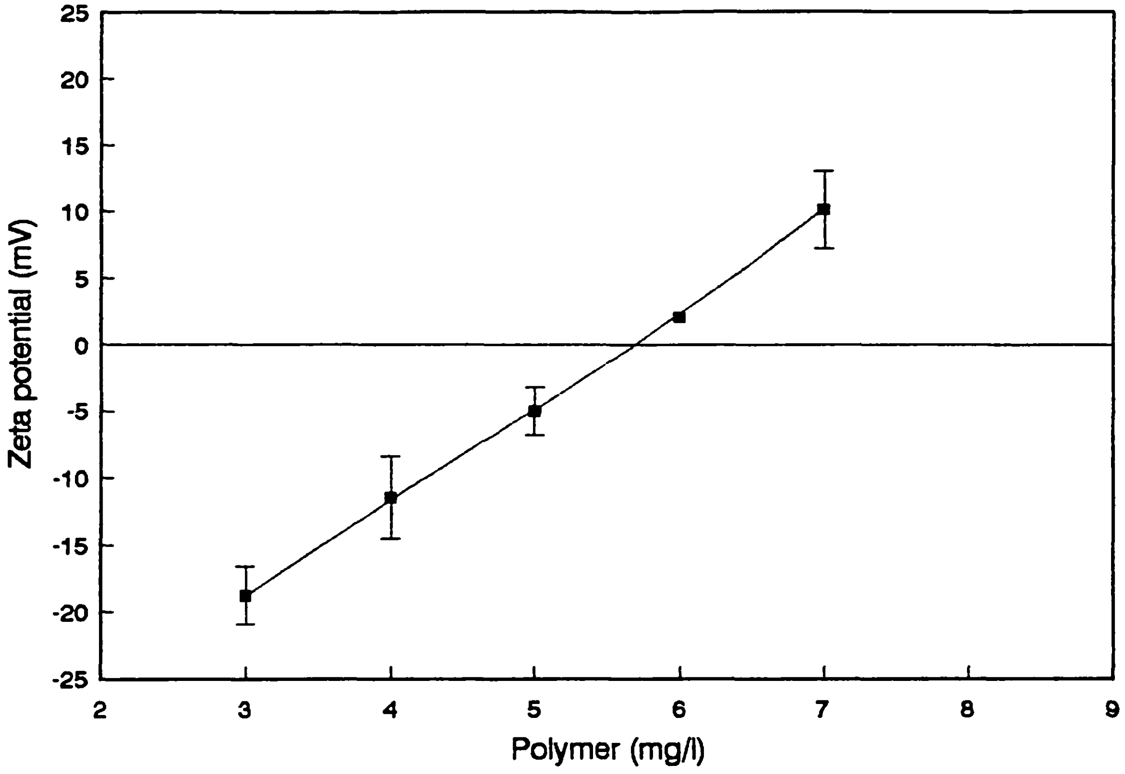
The electrophoretic measurements were performed at a constant electrical potential (*E*) of 80 volts. Only one flat cell was used for all experiments. The dimensions of the cell used and its stationary levels were determined according to the procedure described in the equipment manual. The length of the cell, the distance over which the potential is applied *L*, was approximately 7 cm. Substituting the values of *E* and *L* in equation (5) and (7) they become:

$$U = \frac{V_e}{11.4} \qquad (15)$$

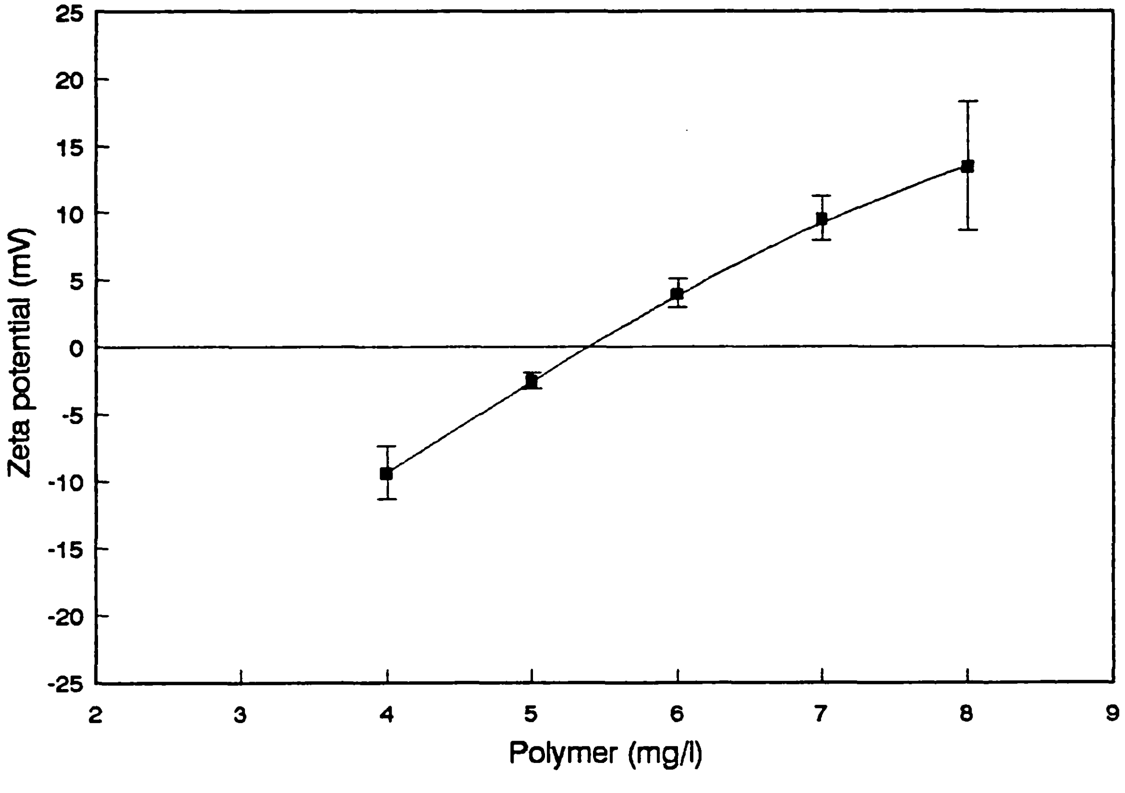
and

$$\zeta = 1.14 \; V_e \qquad (16)$$

Figures 4.12 shows the average Zeta potential and standard deviation values calculated from a number of the electrophoretic velocity determinations performed with the moderate coloured water using 8 and 16 mg/l of alum combined with various polymer doses. Measurements carried out with the high coloured water at various alum-polymer combinations and with the moderate coloured water at higher alum dosages were not successful due to the excessively large size and high settling velocity of the flocs formed.



(a) 16 mg/l of alum



(b) 8 mg/l of alum

Figure 4.12: Zeta potential - Moderate coloured water

The results presented show that Zeta potential values are very low for the range of alum-polymer combinations analyzed, with the zero charge occurring between 5 and 6 mg/l of polymer in both cases. These results, although limited, are very much in agreement with the floc size determination with the maximum floc size corresponding to the minimum floc charge, suggesting that in terms of coagulation-flocculation these are the optimum alum-polymer combinations.

5. DISCUSSION

5.1 Alum as sole coagulant - Jar and filtration tests

The ability of aluminium salts to coagulate humic substances has been well demonstrated in other studies and was confirmed in the present work. Because the aqueous chemistry of aluminium is complex and dependent on the treatment conditions (pH, dose, ionic strength etc) the mechanisms involved in the coagulation process are often uncertain. According to Hundt and O'Melia (1988) the mechanisms of coagulation of humic substances by aluminium salts may include (1) charge neutralization-precipitation, (2) adsorption and (3) simultaneous precipitation. The first mechanism consists of the reaction between soluble cationic species of aluminium and the anionic humic substance. In this case stoichiometry between coagulant dose and humic should exist and restabilization by overdosing should be possible. Adsorption of humic on solid aluminum hydroxide (sweep coagulation) results from physical or chemical forces such as van der Waals interactions, hydrogen bonding, dipole interactions and others. The so called simultaneous precipitation can be considered to be the simultaneous reaction of different humic substances with both soluble Al monomers and polymers and insoluble aluminium hydroxide. The predominance of a coagulation mechanism is directly related to the aluminium species formed upon addition of the aluminium salt to the water.

To better understand the mechanism involved in the coagulation of the synthetic coloured water used in this investigation the results of the jar test with alum (figure 3.5) were plotted in simplified aluminium stability diagram (figure 5.1). From this figure it can be seen that in the coagulation of the moderately coloured water at pH 6, colour removal occurs partially outside, partially inside of the region where precipitation of aluminium hydroxide is likely to occur, suggesting that, whereas adsorption is the main mechanism in the inside region, either charge neutralization or charge neutralization and adsorption occurring simultaneously are the mechanisms responsible for the removal of colour

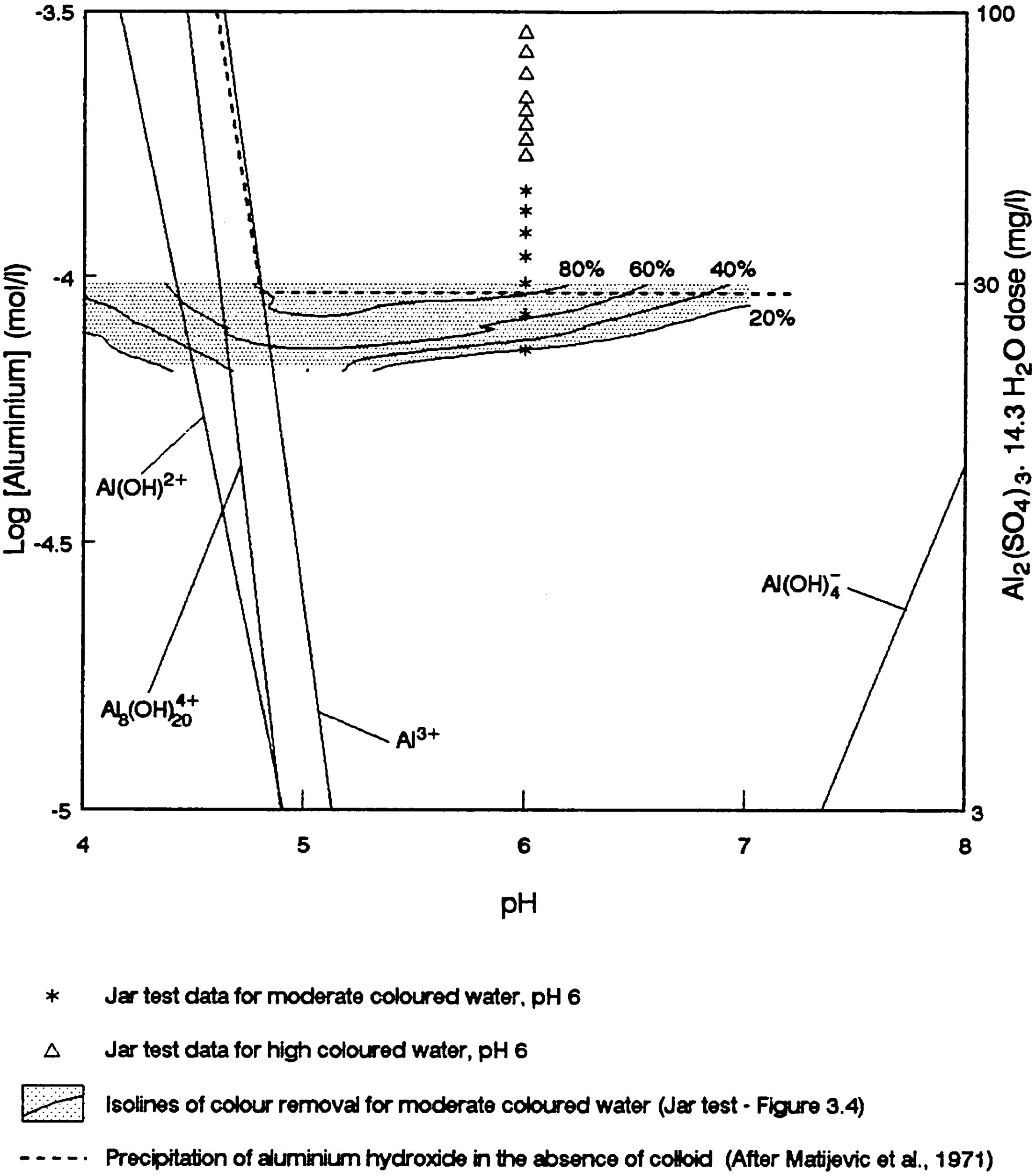


Figure 5.1: Simplified aluminium stability diagram and jar test data points (colour removal > 20%)

in the outer region. It is interesting to note that the optimum coagulation dose (32 mg/l of alum or 30 mg/l as $Al_2(SO_4)_3$ 14.3 H_2O) has occurred very close to the border line. For the more coloured water, colour removal and the optimum coagulation (optimum dose of 80 mg/l of alum or 75 mg/l as $Al_2(SO_4)_3$ 14.3 H_2O) occurs entirely in the region of aluminium hydroxide precipitation, clearly indicating that adsorption of humic on the precipitated aluminium hydroxide floc is the predominant mechanism. The above considerations are consistent with the observations of Dempsey et al. (1984) that between pHs 5 and 6 the predominant mechanism depends on the applied dosage of aluminium.

This difference in mechanisms can possibly explain the deviation in stoichiometry observed in the jar test results for the two coloured waters studied.

The shaded area in figure 5.1 illustrate the effect of pH on the colour removal for the moderately coloured water. The isolines of removal were calculated based on the data presented in figure 3.4.

The jar test is the most common tool used in the prediction of optimum coagulant dosage. Correlation between plant and jar test data is usually satisfactory when a primary coagulant such as alum is used (AWWA Committee Report, 1989). Without questioning the usefulness of the jar test in the optimal dose selection process, the jar and filtration tests results obtained in the present work indicate that care must be exercised when the separation process involved is direct filtration.

A comparison between the jar test results and the filtration performances at 90 minutes (filterability number) for the moderate and high coloured waters (figures 3.5a and 3.5b with figures 3.16a and 3.25a respectively) suggest that the use of the optimum alum dose determined from the jar test will only lead to the optimum filtration if the storage capacity of the filter is enough to deal with the amount of flocs formed in the pre-treatment stage.

For the moderately coloured water, where no quality breakthrough is observed within 90 minutes of filtration, the variation of filtrate quality (average over 90 minutes) with alum dose follows a pattern similar to that observed for the jar test. Because the effect of the head loss in the filterability number was observed to be relatively small, the filtration performance follows the same behaviour of the filtrate quality, which in turn is similar to the residual colour in the jar test. Therefore, one can expect that the optimum dose selected from the jar will coincide or will be very similar to the optimum dose selected from filtration tests, as indeed was observed in this case.

For the highly coloured water, the optimum dose determined from the jar test is considerably higher than the optimum dose determined from the filtration tests. Although the filtration performance again follows a pattern similar to the average filtrate quality, in this case, the variation of filtrate quality with the alum dose does not follow the same behaviour observed in the jar test. In the filtration tests the increase of alum dose leads to an improvement of the filtrate quality only in the early stages of the process. However, because high alum doses are necessary to promote the coagulation of colour and an excessive amount of flocculated material is formed, this improvement is accompanied by a systematic earlier breakthrough that leads the average filtrate quality over 90 minutes of filtration to assume a minimum value (best colour removal) at a dosage well below the optimum coagulant dose selected from the jar test. Since the head loss increases continuously with the increase in the alum dose, it can be expected that the minimum F value will be also obtained at a lower alum dose than that corresponding to the optimum dose for the jar test. It can be observed that the gap between the values of optimum dose selected by each test would be much narrower if the pre-breakthrough filterability number values (37 minutes) were used instead of those calculated at 90 minutes of filtration.

The use of alum as sole coagulant in conjunction with direct filtration proved to be successful for the removal of colour from moderate coloured waters. At the optimum coagulant dose very low levels of colour and residual aluminium can be achieved. At high colour concentrations however the use of alum leads to an excessive amount of flocculated material that results in a unacceptable short filtration run.

5.2 Polymer as sole coagulant - Jar and filtration tests

The destabilization of humic substances by cationic polymeric coagulants is usually described by the mechanism of charge neutralization (Narkis and Rebhun, 1975; Glaser and Edzwald, 1979), where the positively charged polyelectrolyte interacts with the negatively charged groups of the humic substances (mainly $-COO^-$) to form an insoluble precipitate that can be observed as turbidity. The destabilization of humic substances is characterized by the existence of an optimum dose of polymer, or range of optimal doses, whereby both underdosing and overdosing leads to poorer colour (humic) removals.

In the jar tests with both coloured waters (figures 3.6 and 3.7), the appearance of turbidity upon addition of polymer followed the characteristic pattern described in various previous works (Packham, 1973; Narkis and Rebhun, 1975, 1977; Edzwald, 1979; Amy and Chadik, 1983) suggesting that the humic substances present in the water can be successfully destabilized by the cationic polymer used, Magnafloc LT 31. However, no evidence of restabilization was observed within the range of doses applied. Also, a clear optimum dose could not be obtained from the jar test results.

A further attempt was made to determine the optimum dose by measuring the size of the precipitated flocs. The results obtained (figures 4.10 and 4.11) show the existence of a destabilization-restabilization zone at relatively low doses (around the dose corresponding to the peak floc size) and a second region of destabilization (increasing in floc size) at higher polymer doses. The stoichiometry observed in the first region of destabilization, where, by doubling the colour concentration the amount of polymer necessary to produce the maximum floc size is doubled, suggest that the mechanism of destabilization involved is charge neutralization. Confirmation of such a mechanism by measuring the zeta potential could not be obtained owing to the fact that the floc sizes were too small to be observed in the electrophoresis cell available. Indirect evidence that charge neutralization occurs in this zone comes from the fact that when low alum doses are used in combination with polymer to coagulate the moderate coloured water the zeta potential is zero between 5-6 mg/l of polymer, i.e. in the same dose range.

The reasons for the second region of increasing floc size at higher polymer doses is not clear. It is possible that other, non-electrostatic, polymer interactions may exist (e.g. hydrogen bonding) which give rise to floc aggregation by polymer bridging.

The inconsistency between the jar test and the floc size results concerning the existence of a restabilization zone can be due to the use of centrifugation as a separation method.

The size of the flocs formed during polymer coagulation (jar test) indicates that flocculation was very slow, possibly due to the diluted nature of the humic solution and lack of turbidity in the raw coloured waters (low frequency of collisions) or to an inefficient rapid mixing. According to Yeh and Ghosh (1981), if the polymer is not sufficiently dispersed slow mixing does not lead to flocculation, and in their opinion standard jar test apparatus are incapable of providing the necessary velocity gradient for mixing most of polymers of interest in direct filtration.

In contrast to the successful results reported by Edzwald and co-workers (Glaser and Edzwald, 1979; Edzwald, 1979; Scheuch and Edzwald, 1981; Edzwald et al., 1982, 1987) and other researchers, the removal of colour by direct filtration using cationic polymer as sole coagulant in this investigation was not successful (figures 3.12 and 3.23). Although, some colour removal has been achieved the turbidity of the final water was very high and the filtration performance as a whole (filterability number) was very poor when compared with alum filtration. Also, the lack of measurable head loss development indicates that the granular filter was not able to retain the humic-polymer precipitate formed.

Considering that the precipitate material formed in the coiled flocculator has a similar range of particle sizes to the precipitate formed in the jar test (this is not an unreasonable assumption since the turbidity values in the two experiments were similar), i.e. between 0.15 and 0.45 µm for the moderate coloured water and between 0.40 and 0.90 µm for the high coloured water, it is suggested that the lack of removal observed is mainly due to a low contact opportunities between the particle and the surface of the filter grain. By calculating the removal efficiency of a filter bed with porosity 0.40 under 'favourable filtration' (no net repulsive interaction), O'Melia (1985) has shown that there is a range of sizes between 0.1 and 10 microns where particles are difficult to remove due to inefficient transport of the suspended particle from the bulk of the liquid to the surface of the grain. The removal efficiency is a minimum at a particle size of 1 micron.

5.3 Alum-polymer combinations - Filtration tests

It has been demonstrated (chapter 3) that for alum doses lower than the optimum dose a successful coagulation/flocculation of colour can be achieved if a suitable dose of polymer is added in conjunction with alum.

The existence, at each constant alum dose, of a maximum floc size which corresponds to a floc with a zero zeta potential suggests that when the alum and polymer are used as combined coagulants the destabilization of colour occurs mainly by charge neutralization. The fact that the polymer dose corresponding to the maximum size/zero zeta potential does not change significantly with the variation in the alum dose suggests however that possibly only a fraction of the total aluminium added is involved in the charge neutralization process. At the same time, the low concentrations of aluminium present in the filtered water in comparison with the dosage applied indicates that most of the aluminium is removed and therefore is part of the floc formed.

Based on the above evidence and considering that within the range of alum doses used (8 to 24 mg/l) it is likely that both soluble aluminium species and solid aluminium hydroxide are formed when alum is added to the coloured water, it is inferred that whereas the soluble cationic species of aluminium and the polymer are responsible for the destabilization of the dissolved humic, the aluminium hydroxide precipitated provides additional 'targets' for flocculation to occur (remember that only very weak flocculation was observed when the polymer was used as sole coagulant). When the anionic charges of the humic are only partially neutralized by the soluble aluminium and polymer (underdose condition), the aluminium hydroxide may also contribute to the destabilization itself. At lower polymer doses than that corresponding to charge neutralization, the reaction between the humic and soluble hydrolysed species of aluminium and polymer may lead to the formation of low zeta potential colloid that can be enmeshed in the aluminium hydroxide flocs as they are formed and thereby, physically destabilized. This complementary role played by the aluminium hydroxide is consistent with the experimental observation that (i) effective colour removal can be achieved within the polymer underdose region, (ii) the increase of alum dose, and consequent increase in amount of precipitated aluminium hydroxide, widens the range of effective underdose polymer coagulation.

According to the classical filtration theory, particle removal efficiency is dependent on particle transport mechanism and on attachment mechanism (Ives, 1970, 1982). For particles whose size is greater than approximately one micron, particle transport from the bulk of the suspension to the surface of the filter grain increases with the particle size (ignoring density effects). Particle attachment to the grain depends, mainly, upon the magnitude of the electrical double layer interactions between the particle and the filter grain, and the molecular attraction of the van der Waals forces between surfaces (Gregory, 1975). Previous studies (Habibian, 1971; Amirtharajah, 1988) have suggested that effective filtration occurs when the particle are destabilized and exhibit low zeta potentials. The filtration and floc characterization results obtained in chapters 3 and 4 and summarized in figures 5.2 to 5.4 are in agrement with these observations. The maximum floc size entering the filter bed appears to correspond to a zero zeta potential for the floc and to a maximum colour removal and minimum filterability number value (true optimal filtration).

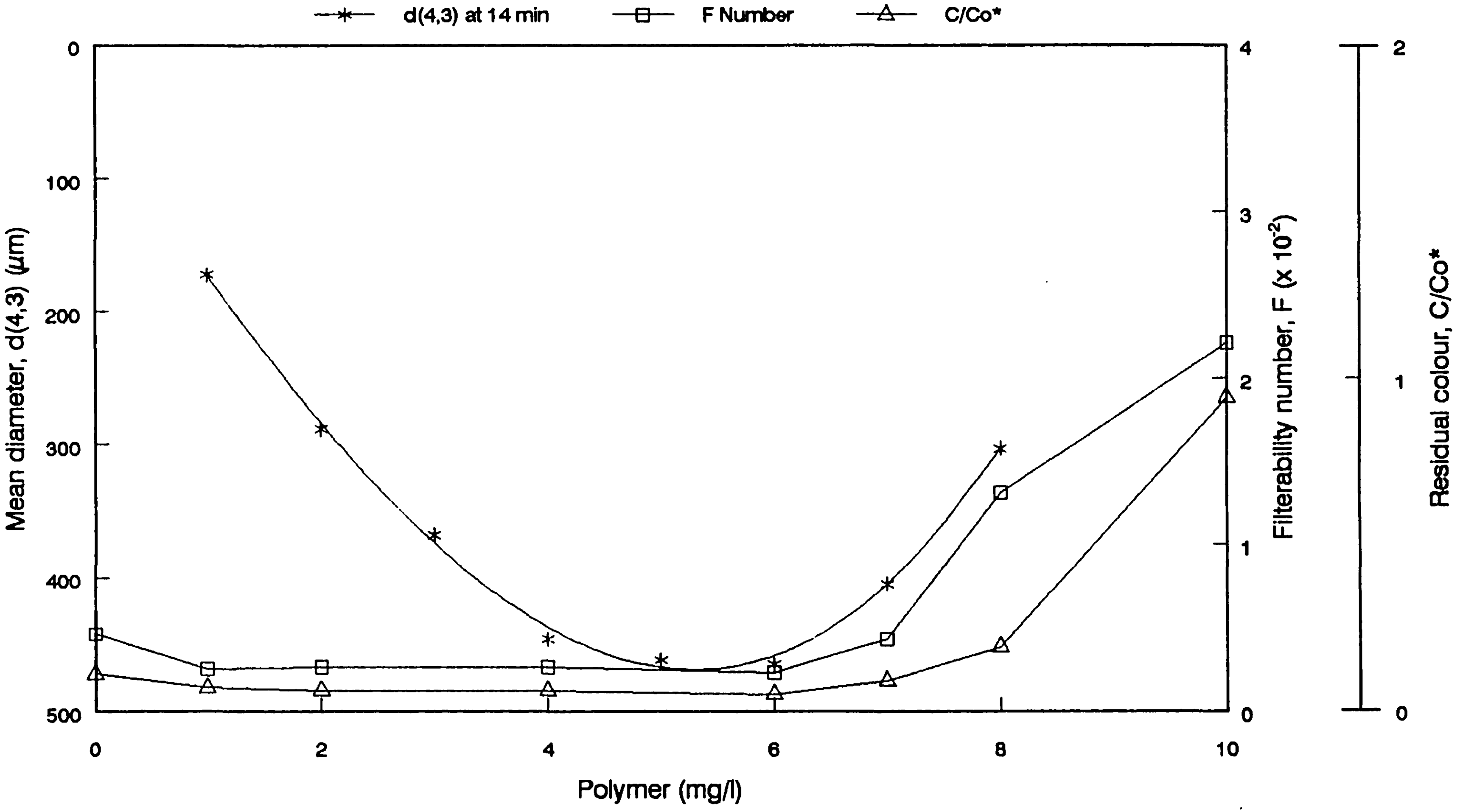


Figure 5.2: Variation of mean floc diameter, filter performance and filtrate quality with polymer dose - Moderate coloured water, 24 mg/l of alum

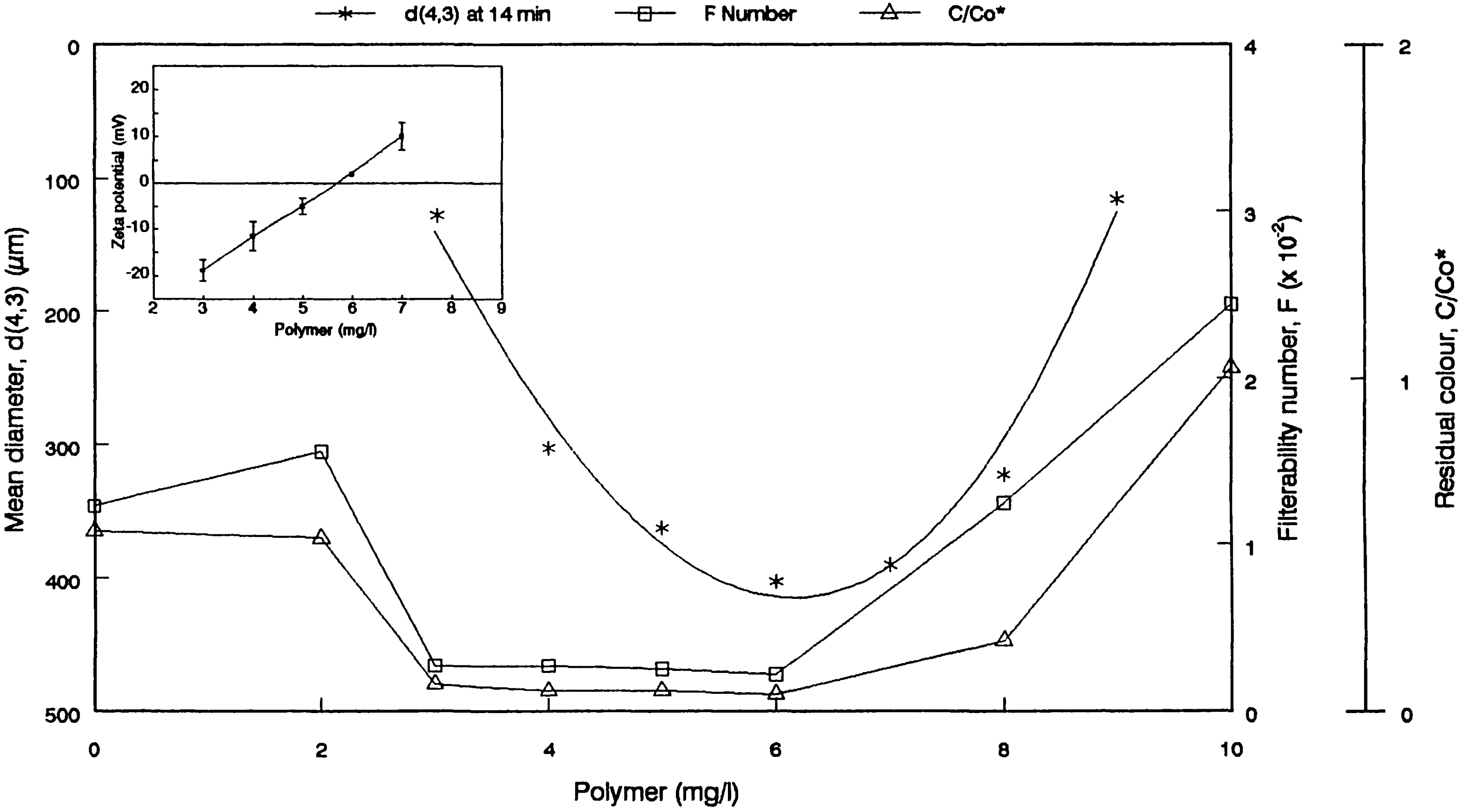


Figure 5.3: Variation of mean floc diameter, filter performance and filtrate quality with polymer dose - Moderate coloured water, 16 mg/l of alum

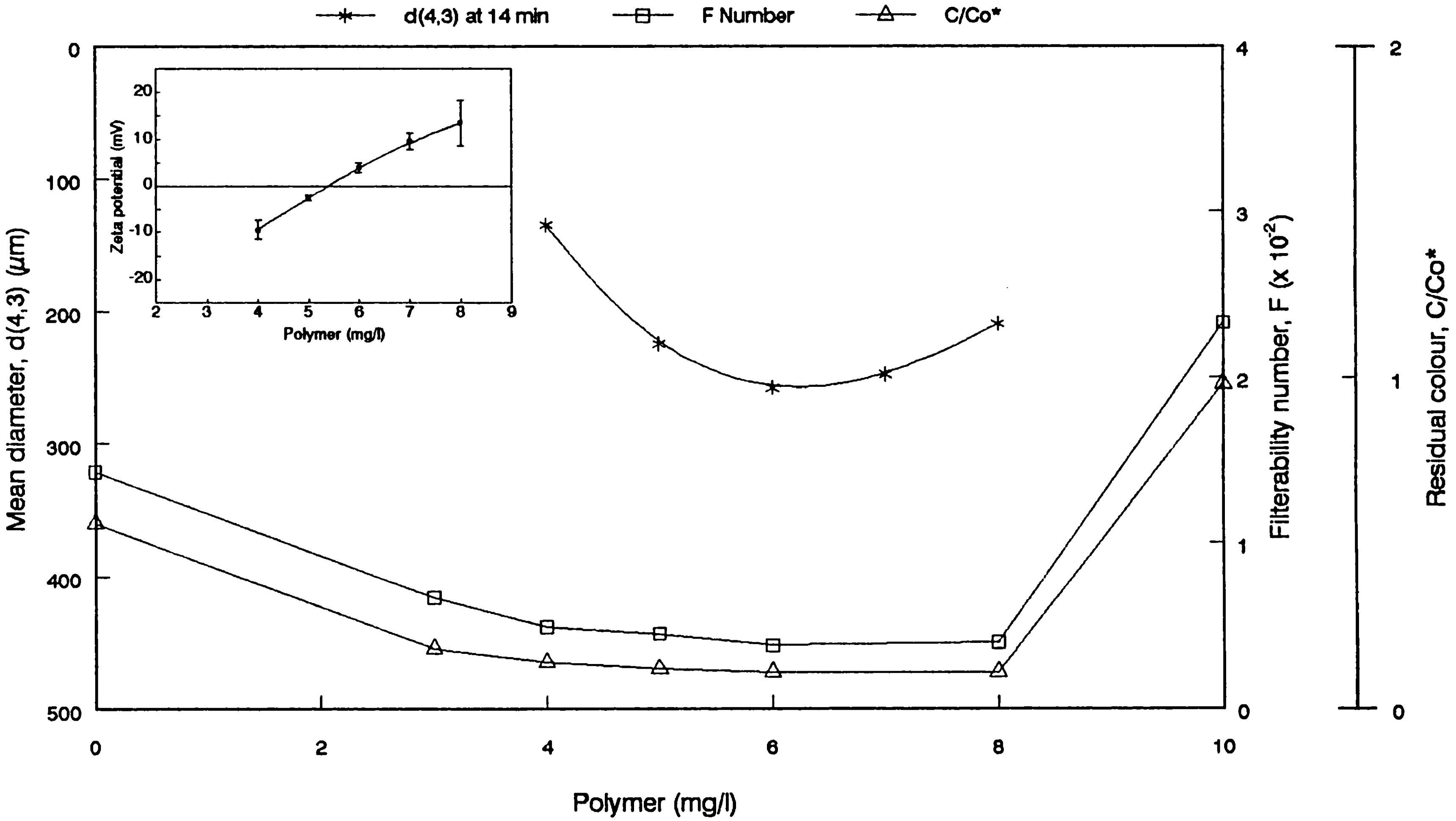


Figure 5.4: Variation of mean floc diameter, filter performance and filtrate quality with polymer dose - Moderate coloured water, 8 mg/l of alum

The relation between floc characteristics and filtration performance (filterability number) at each constant alum dose is clearly different for polymer doses greater, or less than, the polymer dose corresponding to maximum size/zero zeta potential floc. At higher polymer doses, where charge reversal occurs and particle restabilization (characterized by the decrease in size) is observed, filtrate quality and filter performance rapidly deteriorates as the amount of overdosing increases. In contrast, both filtrate quality and filter performance are much less sensitive to polymer underdosing. The reason for this asymmetry in the variation of colour removal and filterability number with polymer dose greater than, or less than, the optimal dose is not clear but it is possible that it may be caused by small amounts of free polymer that coat the filter grains in the very early stages of filtration. The polymer coating favours the attachment of the flocs on the surface of the grain when the net charge of the flocs is negative (underdose) but have an adverse effect on the attachment of the positively charged flocs formed in the overdosing region. In the case of underdose, after the initial stages of filtration ,the free polymer may also help the attachment of the flocs on the previously deposited flocs by means of polymer bridging.

It is clear from the above observations that when using alum and polymer in combination it is not necessary to achieve charge neutralization to obtain a satisfactory filtration performance. A comparison between the filterability number values corresponding to the practical-optimum combinations (section 3.3.2) and those corresponding to the true optimum combinations (figure 5.5) emphasizes this point.

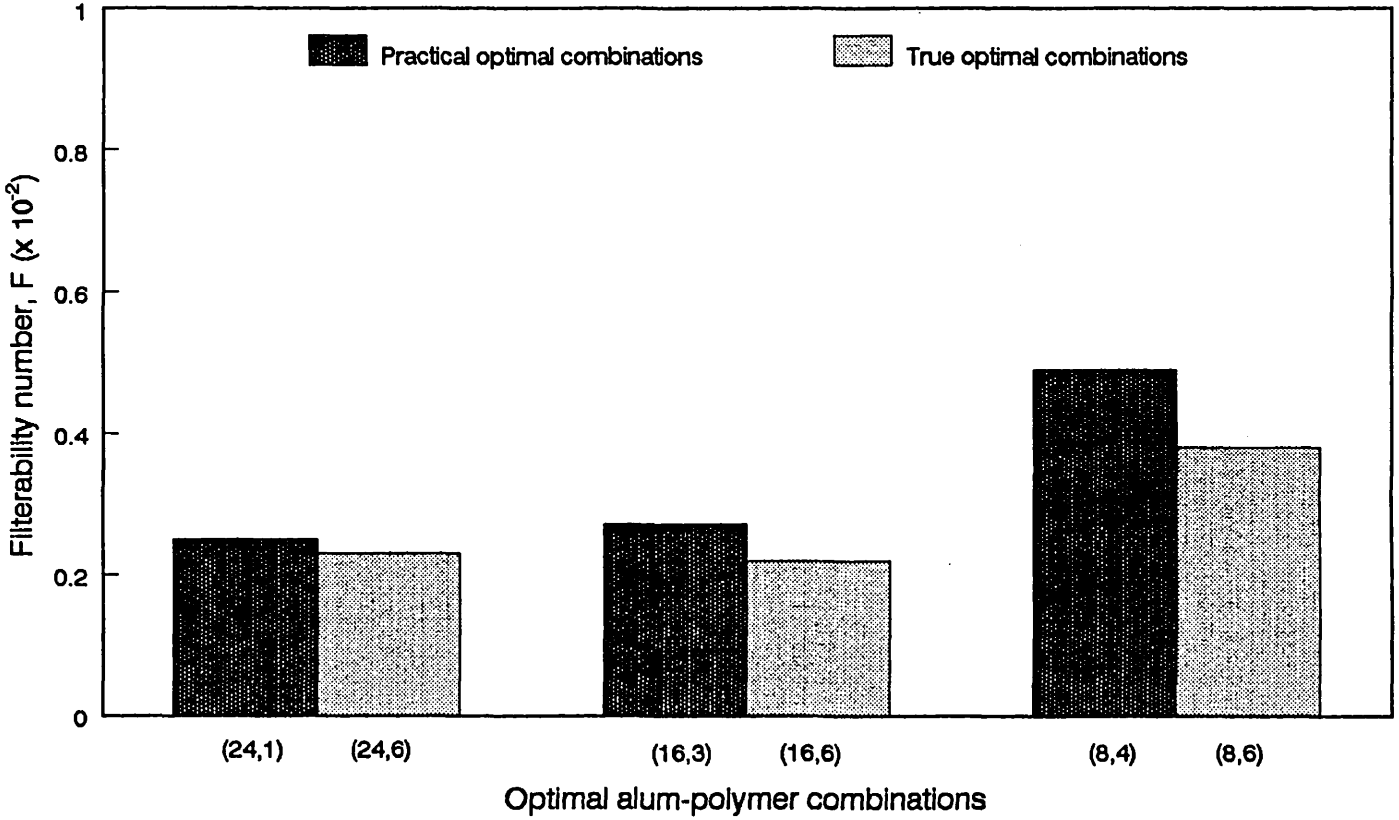


Figure 5.5: Filtration performance at the practical and the true optimum alum-polymer combinations - Moderate coloured water

5.4 Some practical considerations

According to Edzwald and co-workers the applicability of direct filtration in the treatment of coloured waters, and more generally waters containing appreciable amounts of natural organic matter, is limited to those water with total organic carbon (TOC) content less than 5 mg/l (70-90 Hazen units) whether alum or polymer is used as sole coagulant. In the direct filtration of highly coloured water (TOC > 5 mg/l) the use of alum as sole coagulant can lead to effective colour and TOC removal but with an unacceptable short filter run time. Furthermore, the use of a cationic polymer, as an alternative to alum, may be costly and would not produce a treated water of satisfactory quality. In such cases, the use of alternative coagulants, among them alum in combination with a cationic polymer, or conventional treatment is suggested.

For the model filter (0.5 m depth of 0.66 mm diameter ballotini) and pH 6.0 used in this study, direct filtration, using either alum or alum combined with polymer as coagulant, was more efficient in the treatment of the moderately coloured water than the highly coloured one, as can be seen from the calculated filterability number values (figures 3.28, 3.29). Pretreatment using cationic polymer as sole coagulant was shown to be ineffective in producing a reasonable filtrate quality whatever the concentration of colour present in the water.

In the treatment of the moderately coloured water (2.5 Abs. units/m at 400 nm) the filtration using alum alone at the optimum dose proved to be more efficient than any alum-polymer combination, both in terms of filter performance and concentration of residual aluminium. The partial replacement of alum by polymer (designed to reduce the alum dose) was shown to produce no beneficial effect on the performance of the filtration within the filtration time considered.

However, for the highly coloured water (5.0 Abs. units/m at 400 nm), the use of alum as sole coagulant resulted in the production of an excessive amount of flocculated material and an early filtration breakthrough. In this case, the use of an appropriate combination of alum (lower than the optimum dose) and cationic polymer was shown to produce some beneficial effect on the overall performance of the filtration, even though some deterioration in the pre-breakthrough filtrate quality could be observed. The use of low alum doses in the combination resulted in a delay of the quality breakthrough. Also, in contrast to the trend observed for the moderately coloured waters, the reduction of the alum component of the combination has not had a detrimental effect on the residual aluminium concentration.

From these results, it seems that, for a given filter bed, the partial replacement of alum by cationic polymer does not offer any substantial advantage (cf. alum at optimum dose) in the treatment of low to moderately coloured waters, but may be a suitable alternative in the treatment of highly coloured waters. It is thought however that the use of combined alum and polymer in the pretreatment for direct filtration may have its major application in the case of existing plants, normally operating at low colour concentrations and using alum as sole coagulant, which experience operational difficulties (unacceptable short filter runs) when dealing with periodic and substantial, short-term, increases in the concentration of colour. During these occurrences a sensible partial replacement of alum may lead to longer filter runs whilst maintaining acceptable filtrate quality.

6. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary and conclusions

The following topics are a summary of the main observations and conclusions obtained in the reported investigation about the alum-cationic polymer interactions in the direct filtration of coloured waters:

i. Reverse osmosis followed by freeze drying proved to be an efficient method of concentrating humic substances from natural waters. High volumes of waters can be processed in a relatively short time. Reconstituted waters prepared from reverse osmosis-freeze dried extracts were shown to behave similarly to natural coloured waters.

ii. At pH 6 the mechanisms involved in the coagulation of the reconstituted coloured water by aluminium sulphate depends on the alum dose applied. At high alum doses it appears that the main mechanism is the adsorption of colour on the precipitated aluminium hydroxide floc, while at lower alum doses charge neutralization alone or in conjunction with adsorption may be responsible for the destabilization of colour.

iii. This study has demonstrated that moderately to highly coloured waters can be successfully destabilized by the combined use of alum (at lower doses than the optimum dose) and a cationic polyelectrolyte. For a constant alum dose, maximum flocculation occurs at or near the polymer dose that corresponds to the zero zeta potential floc.

iv. Experimental evidences suggest that charge neutralization is an important mechanism when alum is used in combination with cationic polymer to coagulate organic colour. It is believed that in this system the soluble cationic species of aluminium together with cationic polymer are responsible by the destabilization of colour, whereas the precipitated aluminium hydroxide may provide additional targets for flocculation. When the system is underdosed in relation to the cationic polymer, the precipitated aluminium hydroxide may also contribute to the destabilization itself through physical enmeshment or adsorption of the partially neutralized colour. Polymer overdose (cf. polymer dose for charge neutralization) leads to particle restabilization.

v. For the fine mono-layer model filter (0.5 m depth of 0.66 mm diameter ballotini) used in this investigation, direct filtration, using either alum or alum combined with polymer as coagulant, was more efficient in the treatment of the moderately reconstituted coloured water than the highly coloured one. For the highly coloured waters, good filtrate quality can be achieved at the initial stages of the filtration but the formation of excessive amounts of flocculated material generally leads to an early breakthrough. The use of low alum doses - supplemented with cationic polymer - in this case was shown to produce longer filtration runs.

vi. When alum-polymer combinations are used in the pretreatment of coloured waters, it is not necessary to achieve charge neutralization to obtain a satisfactory filtration performance. For constant alum doses, practical-optimum filtrations are generally achieved with polymer doses in the underdose range, i.e. negatively charged flocs. It is speculated that there may be small amounts of free polymer that enter the filter during filtration which adsorb on the filter grains or previously deposited flocs and thereby increase the attachment efficiency.

vii. In this study, a linear relationship between colour concentration and dose of coagulants (alum-polymer combinations) required to produce relatively similar filtration performance was observed.

viii. Low concentrations of residual aluminium can be achieved at the optimum alum, or alum-polymer combinations, if effective removal of the flocculated material is obtained during filtration.

ix. Ives' Filterability Number proved to be a useful tool in the evaluation of the effects of different alum-polymer combinations on the filtration performance. For the filter model used, the filterability number was more sensitive to changes in filtrate quality than to head loss.

6.2 Recommendations for future works

In view of the fact that the present work offers evidences that the destabilization/coagulation of moderately to highly coloured waters can be successfully achieved by the combined use of alum and a cationic polymer, and that the main problem faced in the use of direct filtration as the separation method is the formation of excessive amounts of flocculated material, the investigation of the following aspects are suggested:

(i) The effect of coagulating the colour at low pH values in the overall performance of the direct filtration;
(ii) The effect of reducing and/or eliminating the flocculation period in the overall performance of the filtration;
(iii) The use of coarse media and dual media direct filters;
(iv) The use of different cationic polymer types.

In such studies the use of Ives' filterability number for the evaluation of filtration performance is recommended. However, for the best results in the use of this index, its calculation at the filtration breakthrough time is suggested. If humic substances (coloured water) availability is a constraint, and longer filtration runs are not possible, the use of shorter filter models may be advisable. The residual coagulant content may also be used as a complementary parameter in the evaluation of the overall filtration performance.

The investigation of the effects of both turbidity and mixing conditions in the coagulation/flocculation of humic substances (colour) by cationic polymers as sole coagulant is also recommended.

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