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Master's Thesis

**The Use of Organic Polymers in the Chemical Purification of Peat
Derived Runoff Water**

In Oulu 20.03.2013

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Acknowledgements

Foremost, I would like to express my sincere gratitude to my supervisor Prof. Bjørn Kløve, my advisors Elisangela Heiderscheidt and Ana-Kaisa Ronkanen for their continuous support, patience, motivation, enthusiasm, and immense knowledge. They worked relentlessly to see me through the research and writing of this thesis. My sincere thanks also goes to MVTT r.y for their financial support in the realization this work.

Special thanks go to Jaakko Saukkoriipi of the Finnish Environmental Institute – SYKE, Epie Kenedy of the Department of Agriculture, University of Helsinki, Meseret Walle and Justice Akanegbu of the Water Resource Laboratory and Tiomo laboratory technician, Water Resource Laboratory, University of Oulu for their encouragement, insightful comments and hard questions.

Last but not the least I would like to thank my family: my dad Dr. Ngakfumbe Simon (late 1942 – 11.02.2013), my kids Etonde, Jr Njeba and Berry, my sisters and brother, my in-law Bungong Kwalar, my nieces: Nyuito and Rinyui. Though far away your relentless prayers, moral and financial support kept me going, I miss you all dearly. Special appreciations go to Jones Karawa and his family for supporting me morally and spiritually. My sincere thanks also go to Anong O. Patience for her steadfast moral, spiritual and financial support.

Faculty of Technology

Department Process and environmental engineering		Degree Programme (Master's thesis) or Major Subject Water resources and environmental engineering laboratory	
Author Ngakfombe, W. Joseph		Thesis Supervisor Klove, B., Professor	
Title of Thesis: The use of organic polymers in the chemical purification of peat derived runoff waters			
Major Subject Water resource management	Type of Thesis Master's Thesis	Submission Date 20.03.2013	Number of Pages 66
<p>Abstract</p> <p>In our present day wastewater management have a high influence on the quality of our environment, its neglect or poor treatment can lead to very negative effect on our bio-diversity and the environment in general.</p> <p>This study seeks to address the limitations of using inorganic coagulants in the treatment of peat runoff water by evaluating the efficiency of organic polymers as coagulants agents in the chemical purification process. The limitations of inorganic coagulants include; discharge of residual metals into downstream waters, over dependence on pH, high dosage and high sludge production.</p> <p>For our experiments two cationic organic polymers epichlorohydrin/dimethylamine (pAMINE) and polydiallyldimethyl ammonium chloride (pDADMAC) were selected based on their molecular weight and charge density. Polyferric sulfate (PFS) which is the pre-hydrolyzed metal salt coagulant presently being used at several peat extraction treatment sites in Finland was also tested.</p> <p>The optimum dosage requirements of the tested coagulants were determined based on turbidity removal. The dosage requirement of the coagulants were considerably different; optimum dosages of PFS ranged from 190 mg/l to 200 mg/l while that of the organic polymers ranged from 40 mg/l to 60 mg/l for pAMINE and 70 mg/l to 90 mg/l for pDADMAC. Where optimum dosages were applied removal of turbidity ranged from 85 % to 95 %. PFS presented better overall performance in the removal of TOC about 80 % against less than 40 % for both organic coagulants. pAMINE leached nitrogen into the system, the leaching diminished in tests at low temperature.</p> <p>The evaluation of the influence of mixing on the coagulants performance revealed that PFS's performance is more sensitive to variation in mixing than the organic coagulants. Optimum values for fast mixing intensity were over 100 rpms for all tested coagulants with no improvement or detrimental effects observed for values up to 400 rpm. Optimum observed fast mixing time was 10 s for all coagulants. Best slow mixing speed and time were achieved at above 20 rpm and above 10 minutes for all tested coagulants.</p> <p>Organic polymers and inorganic coagulants alike showed lower dosage requirements with lower pH values, pAMINE achieved purification efficiency at dosages as low as 30 mg/l and pDADMAC was less affected by low pH achieving acceptable turbidity removal at dosages of less than 60 mg/l. PFS dosage requirements dropped by as much as 45 % from 200 mg/l at pH 6.5 to 120 mg/l at pH 4.5</p>			
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Symbol and abbreviations

AL	aluminium
C	Color (mg/l Pt)
C_0	Initial concentration of particles in suspension
COD	Chemical oxygen demand
DOC	dissolved organic carbon
Fe	Iron
g	Acceleration due to gravity (cm/s^2)
G	Velocity gradient (s^{-1})
L	length of rectangle basin (m)
n	Mixer rotational speed (revolution per second)
NOM	Natural organic matte
PO_4	Phosphate phosphorous ($\mu\text{g/l}$)
Q	Flow rate (m^3/s^1)
rpm	Revolution per minute
SS	Suspended solids
t	Retention time (s)

T	Turbidity (NTU)
t_i	Elapsed time (s)
TOC	Total organic carbon
T.P	Total phosphorous ($\mu\text{g/l}$)
T_t	Turbidity at time t (NTU)
v	Horizontal flow velocity (m/s^1)
V	Volume of tank (m^3)
P	Power (W)
μ	Absolute velocity (N.s/m^2)
AlCl_3	Aluminium chloride
RT	Residual turbidity (NTU)
MV	molecular weight (mol)
CD	Charge density (meq/g)
TSS	Total suspended solids
T.N	Total nitrogen ($\mu\text{g/l}$)
C_i	Initial color

Tt ₀	Turbidity measure minutes a minute before the end of flocculation time(NTU)
Ti	Initial turbidity
Av	Average
PFS	Polyferric sulphate
pAMINE	Epichlorohydrin-dimethylamine-copolymer
pDADMAC	Poly-diallyldimethylammoniumchloride

1 Introduction

Today more than ever before there is a dire need to protect our natural resources and ensure the wise and sustainable use of our environment. Like every other human activity, peat extraction has always been of great interest to the public, governments and environmental organizations (Canadian Peat Harvesting and the Environment, 2001).

Peat is an important source of energy in Finland, and it is therefore of high economic importance. The Association of Finnish Peat Industries (2010), estimates that 17 % to 20 % of combined heat and power energy in Finland is produced from peat, it is also been used as a growing medium in horticulture, as frost insulation, absorbent peat, composting peat as well as landfill structure and improvement.

Though peat extraction is very important to the Finnish economy, it also has environmental drawbacks; peat extraction involves removing of the natural vegetation, landscape alterations, changing of hydrological balance, nutrient load, noise and dust emission, and this will in turn lead to the disappearance and changing of biodiversity (Sopo, et al., 2002). Peat extraction has dramatically altered and modified the surface topography and vegetation of the pristine peatlands. The drainage of peatlands for peat extraction and other activities such as forestry and agriculture are a cause for concern (Seters and Price, 2001).

One environmental impact related to peat extraction and usage is increased greenhouse gase emissions. WWF, 2008 equates the emission of carbon dioxide from peat burning to that from the transport sector estimated at 10 million tons per year. The formation of peat takes place in wetlands with high water table under anaerobic conditions. Lowering of water table during peat extraction quickens decomposition processes of organic matter releasing carbon dioxide which is a main greenhouse gas (Canadian Peat Harvesting and the Environment, 2001). On a global basis, combustion of peat as a fuel releases three times the quantity of carbon as is released from drained peatlands, on the other hand, the release of methane from un-drained peatland has a greater impact than

the combined total from areas used for peat combustion and other drainage (Gorham, 1991).

One of the most significant negative impacts of peat extraction is that it has a major effect on downstream aquatic ecosystems. The leaching of pollutant substances and the increase in runoff water volume will inevitably negatively influence the physical and chemical quality of the receiving water bodies (Klove, 1997, 1998, 2000; Canadian Peat Harvesting and the Environment, 2001). Fresh water quality one of vital natural resource is seriously loaded by pollutants from our domestic, industrial, and agro-industrial activities sectors. Sustainable management of this resource should be our utmost priority in order to guarantee it stays renewable (Jern, 2006 pp. 1). Due to the detrimental effects of peat extraction discharging waters, it is important that purification methods are developed and optimized to fit the unique condition required. Peat extraction areas are generally isolated in areas where in most cases electricity is not provided, hence for purification methods to be feasible they need to be simple, inexpensive and low maintenance while efficient. Of particular interest is the removal of organic matter, nutrients and suspended solids from the discharging water. Amongst the numerous water and wastewater purification methods; sedimentation basin, overland-flow areas, chemical purification and others, chemical treatments though expensive is a well-known method and it is required for sites where water quality is crucial. Chemical purification is considered by the Finnish authorities to be one of the best available technologies for the treatment of peat extraction runoff water (Association of Finnish Peat Industries, 2010).

Chemical treatment using metal salts of iron and aluminum has long been applied in several peat extraction sites in Finland. Nevertheless, variations in incoming water quality and lack of optimization of treatment facilities have resulted in significant variations in purification efficiency and increase in metal residual in the discharge water (Heiderscheidt, 2011). The goal of this study is to develop the chemical purification method by evaluating the efficiency of organic polymers as coagulant agents in the treatment of peat extraction water and therefore provide an alternative to metal salt

coagulants. The advantages of organic polymers coagulants include, (Bratby, 2006, pp 194; SNF FLOERGER)

- reduced dissolved salt in treated water
- less sludge bulk with no metal hydroxide precipitate
- less reliance on pH
- lower dosage compared with inorganic salts coagulants

The aim is to test under laboratory conditions the purification efficiency achieved by selected organic coagulants while comparing their performance with the widely used metal salt coagulant (polyferric sulphate). Furthermore, to identify the required coagulants dosages, mixing requirements and sedimentation characteristics. The influence of temperature and pH in purification efficiency, and sedimentation characteristics of tested coagulants are also evaluated.

Laboratory experiments were performed using the jar test laboratory procedure and the polymers used were Epichlorohydrin-dimethylamine-copolymer (pAMINE) and Poly-diallyldimethylammoniumchloride (pDADMAC) cationic polyelectrolytes. These polymers (pAMINE and pDADMAC) are normally used in water treatment because of their low molecular weight (MW) and high cationic charge. The inorganic metal salt, polyferric sulphate (PFS) was also tested as control. The purification efficiencies were then evaluated based on the percentage removal of pollutant substances such as: total nitrogen (T.N), total phosphorous (T.P), suspended solids (SS), total organic carbon (TOC) and phosphates (PO_4).

2 Chemical treatment

The processes involved in chemical treatment of both wastewater and portable or drinking water treatment are mainly coagulation, flocculation and sedimentation. Coagulation is an essential mechanism in the removal of suspended colloidal particles mostly responsible for turbidity, color, taste and odor. Coagulants are responsible for the formation of small scattered particles which come together into larger and more stable particles flocs. These then settle as sediments and can be removed (Bratby, 2006; Tzoupanos and Zouboulis, 2008; SNF FLOERGER).

2.1 Processes in chemical treatment

2.1.1 Coagulation

Coagulation is the first stage in chemical water treatment and it is meant to neutralize the electric charges in the particles destabilizing the colloidal suspension and cause the particles to agglomerate, the particles can be mineral, organic and biological in nature (SNF, FLOERGER).

Aluminum and iron based metal coagulants are the most commonly used, these include ferric sulfate, ferrous sulfate, ferric chloride and aluminum sulfate, aluminum chloride and sodium aluminate for iron based and aluminum based respectively. Low cost and availability of metal coagulant favors its wide spread use (Bratby, 2006 pp. 32; Tzoupanos and Zouboulis, 2008). Their high dependence on pH, high dosage requirement, vulnerability to temperature variation and high sludge stand as the drawbacks to their use (Tzoupanos and Zouboulis, 2008). Addition of these salts into raw water results in dissociation of the salts to give their trivalent ions, which hydrates to give complex water molecules $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and $\text{Fe}(\text{H}_2\text{O})_6^{3+}$. A series of reactions then lead to the replacement of H_2O molecules by OH^- ions to form soluble $\text{Al}(\text{OH})^{2+}$ and $\text{Fe}(\text{OH})^{2+}$ which are effective as coagulants due to their ability to strongly adsorb on the surface of most negative colloids (Bratby, 2006 pp. 42).

There has been considerable research on the use of prehydrolyzed inorganic coagulants and its effectiveness as primary coagulants, they include; polyaluminum chloride, polyaluminum silicate chloride and polyaluminum chloride. Their primary advantage is that they are not very dependent on raw water pH and temperature. (Bratby, 2006 pp. 38-39).

Coagulation mechanisms for organic polymers

According to Bratby, (2006) there is no single mechanism of destabilization by polyelectrolytes which can be considered the main mechanism. In all instances however two key mechanisms do stand out which may operate in opposition, conjointly, or one mechanism clearly predominating over the other. These are referred to as the bridging mechanism (Figure 1) and the electrostatic patch mechanism;

- a. The bridging model; where polyelectrolytes segments are adsorbed on the surfaces of adjacent colloids, binding them together.
- b. Electrostatic patch model; oppositely charged ionic polyelectrolytes to the suspended material are adsorbed and thus reducing the potential energy of repulsion between adjacent colloids.

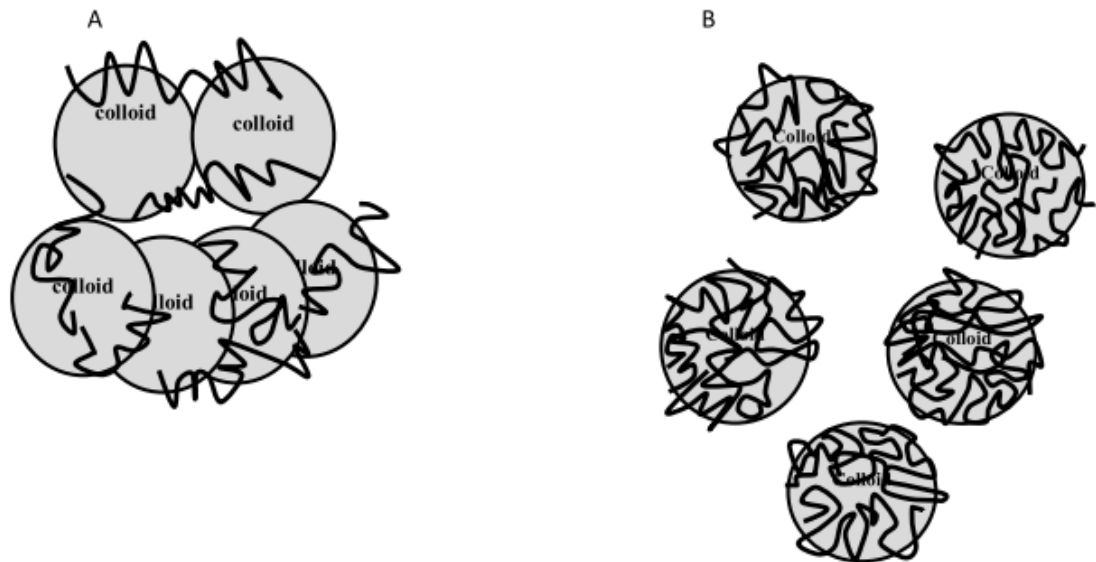


Figure 1. Schematic picture of (a) bridging flocculation and (b) restabilisation by adsorbed polymer chains (Modified from Bolto and Gregory, 2007).

2.1.2 Flocculation

The flocculation process is one of the main stages in water and wastewater treatment. It occurs when destabilized particles from the coagulation stage are mechanically induced to agglomerate into compact and fast settleable particles commonly called flocs. The agglomeration of the particles is due to velocity difference or gradient in the previously coagulated water. The agglomerates or flocs are ultimately removed by sedimentation or in some cases floatation (Bolto and Gregory, 2007).

Flocculation process is generally classified into two separate processes; perikinetic and orthokinetic flocculation. Perikinetic flocculation is the process that is caused by the collision of colloidal particles (Brownian motion of particles). Perikinetic flocculation is completed within seconds and it initiated soon after the destabilization of particles.

On the other hand orthokinetic flocculation is the process that starts once the perikinetic flocculation is completed. It is flocculation due to contact of colloidal particles resulting

from induced bulk fluid motion. (Bratby, 2006; Vigneswaran and Visvanathan, 1995) According to Bratby (2006), velocity gradient is inversely proportional to floc size and directly proportion to particle contact, there is therefore a limiting flocculation time beyond which floc particles will stop growing, Bratby (2006) again states that “*the lower the velocity gradient, the longer will be the time needed to reach the optimum floc size, but the larger will be the final floc size*”.

2.1.3 Sedimentation or settling

Settling is a physical separation (solid-liquid separation) process with the clarified supernatant water on top and concentrated sediments at the bottom of the tank. The purpose of sedimentation is to remove coarse suspensions, coagulated or flocculated impurities and precipitated impurities of chemical treatment and settle them at the bottom of the tank (Hammer Jr, 2008 pp.213). Types of sedimentation include (American Water works Association, 1990);

- a. Settling of discrete particles; individual particles will sediment without coming in contact with bordering particles.
- b. Flocculent particles; particles will agglomerate and increase in size due flocculation thereby increasing in mass and as such settle faster.
- c. Zone settling; particles may settle en-mass as a unit with individual particles maintaining a fixed position with respect each other as they settle.
- d. Compression settling; this will occur where particles concentration is so high that sedimentation can only be achieved through compaction.

The quality of supernatant water depends on certain parameter such as temperature, pH, mixing, and dosage and their effects on the optimum condition (Gregory and Duan, 2001).

2.2 Parameters influencing purification efficiencies

2.2.1 Influence of temperature

Higher temperature quickens the rate of chemical reactions; Arrhenius 1889 cited in Hammer Jr, 2008 states the relationship between the rate of reaction and temperature as;

$$k_2 = k_1 Q T^2 \quad (1)$$

Where k = reaction rate constant at respective temperature T (1/day)

Q = temperature coefficient, dimensionless

T = temperature, ($^{\circ}\text{C}$)

Low temperatures are known to stabilize colloidal surfaces and to reduce the rate of hydrolysis reactions which in turn causes a decrease in particle recovery (Yu et al 2006). High temperatures results in lower viscosity of water and free movement of particles as well as higher reactions kinetics and higher solubility of applied chemicals (Bradtby, 2006 pp171-172).

Heiderscheidt et al (2013) showed that when temperature was lowered from 20°C to 5°C the purification efficiency of metal salt coagulants were reduced with varying degree; it resulted in the decrease of the removal percentage of T.N and TOC by about 10 %, the most affected was the removal of SS with a reduction of up to 60 %, the lowering of the temperature also adversely affected the rate of settling of all the metal salt coagulants.

2.2.2 Influence of pH

The performance of metal salt coagulants is known to be highly dependent on the pH of the water compared to organic coagulants, according to Baghvand et al., (2010) working with alum and ferric chloride at a pH range of 4 – 8 they found out that the best pH for optimum results was between 5 and 6 for ferric chloride and 6 and 7 for alum.

With cationic polyelectrolytes, humic acid precipitation is directly proportional to pH due to lower negative charge presented by these substances; this is caused by a decline in the degree of ionization. Narkis and Rebhun (1975 and 1977 cited in Bratby 2006) observed that a drop in pH from 6.0 to 2.8 sees a drop in the best dosage requirement of the polyelectrolyte from 3.0 mg/l to 0.8 mg/l.

The addition of metal salt coagulants will significantly affect the pH of the solution, according to Heiderscheidt (2011, pp 47 - 65) the pH of raw water range between 5.8 - 6.8 and after treatment they ranged from 3.5 – 4.8 showing a significant drop in the pH range due to the treatment with metal salt coagulants. This is not the case with organic coagulants, according to Bratby 2006 pp194 organic polymers do not require too much adjustments in pH.

2.2.3 Influence of mixing

An important parameter in the treatment of water and wastewater is the fast-mixing which is when coagulants are added to the water and require turbulent mixing, so that they can be circulated rapidly and uniformly through the mass of the water. The lack of fast mixing can cause the coagulants to perform poorly due to regional under and over dosing (Kan et al, 2001). Slow mixing comes soon after rapid mixing and it is intended to introduce particle contact and growth of primary flocs formed during rapid mixing (Rossini et al, 1998).

Heiderscheidt (2011, pg. 75) shows the optimum mixing speeds for tested solid and liquid metal salt coagulant on various raw water samples ranges from 50 - 90 rpm for slow mixing speed and 100 - 400 rpm for fast mixing speed. The optimum mixing times ranged from 15 - 25 minutes for slow mixing time and 10 - 60 seconds for fast mixing time, mixing parameters applied during the flocculation phase were found to be more significant than that applied during the coagulation phase.

As mixing proceeds, there is point to point and time variation in the fluid velocity, the parameter stating mixing strength is identified as velocity gradient or simply G-value (Rossini et al., 1998);

$$\text{Where } G = (P/\mu V)^{1/2} \quad (2)$$

Where:

G = Velocity gradient for rapid mixing (s)

P = Power (W)

V = Channels volume (m³)

μ = absolute velocity or dynamic water viscosity (N.s/m²)

2.2.4 Influence of Dosage

The dosage administered in a chemical treatment would affect the purification efficiency of all coagulants. There is a rapid drop in turbidity with increase in dosage, this will often peak at the optimum dosage and in most cases further increase after optimum dosage will not change the residual turbidity of the treated water. In other cases the further increase in dosage can cause charge reversal and re-suspension of particles causing increase in turbidity values (Heiderscheidt et al., 2013, Yu et al., 2006, Baghrand et al., 2010). Increase in initial turbidity results in decrease in turbidity removal. According to Baghrand et al., (2010), working with alum; a fixed dosage of 10 mg/l at pH 7 and initial turbidity of 10 NTU achieved a residual turbidity of about 0.1 NTU, at 100 NTU the achieved residual turbidity was about 2 NTU, at initial turbidity of 200 NTU the achieved residual turbidity was about 40 NTU, at 500 NTU residual turbidity was up to 70 NTU and at 1000 NTU it was about 180 NTU. Ferric chloride was less affected by initial turbidity, at pH 5 and dosage of 10 mg/l ferric achieved residual turbidity of 0.1 NTU at initial turbidity of 10 NTU, about 2 NTU residual turbidity was achieved with initial turbidity of 100 NTU, residual turbidity of about 15 NTU was achieved with initial turbidity of 200 NTU and about 70 NTU residual turbidity with an initial turbidity of 1000 NTU.

3 Organic polymers

Polymers are a variety of natural or synthetic water soluble compounds whose molecules are held together by repeating covalent bonds (Bratby, 2006). Their use as primary coagulants will better eliminate turbidity; they can greatly enhance processes in potable water and wastewater treatment by wholly or partially replacing inorganic coagulant (Lee et al., 1998; SNF FLOERGER). Organic polymers are generally classified based on the electric charge they carry due to ionization of functional groups; positively charged or cationic polymers, negative charged or anionic polymers and those with no charge are termed non-ionic polymers. Charged or ionic polymers are generally called polyelectrolytes (Bolto and Gregory, 2007; Lee et al., 1998; Bratby, 2006).

3.1 General characteristics of polymers

The major characteristic of polymers that determines their use as coagulant or flocculant aid is their molecular weight (MW) and their charge density (CD). The polymer MW is the sum of the molecular weights of the individual repeating chemical units called monomers. MW of polymers can range from 10^4 - 10^7 and they are classified into low, medium, and high molecular weights which represent less than 10^5 , between 10^5 – 10^6 and more than 10^6 respectively (Bolto and Gregory, 2007).

Molecules of polymers are represented in a coil formation. The coil size depends on the CD of the ionized molecule. The coil formation and the distance (r) a measure of the size of the molecule are presented in Figure 4. Besides the size of a molecule of a polymer being dependent on the MW and CD, it also depends on the ionic strength of the receiving medium. Figure 5 shows decreasing ionic strength of a cationic polymer when it is introduced into an anionic medium.

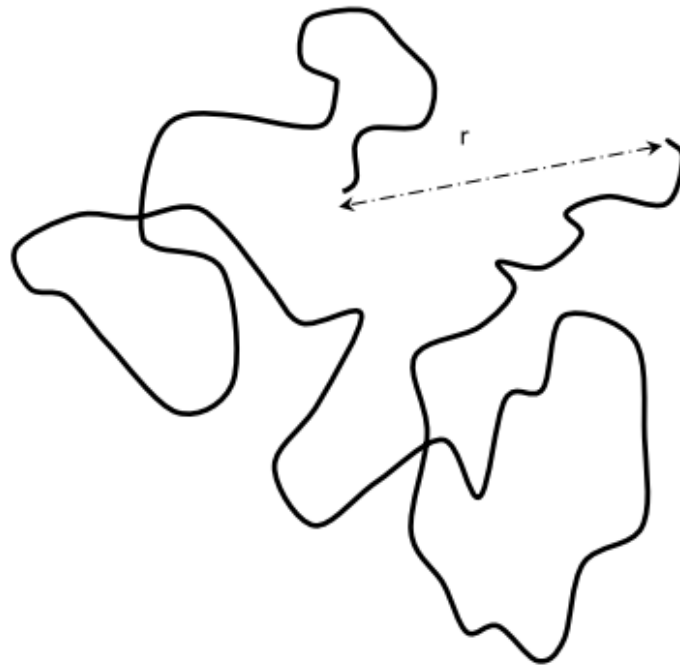


Figure 4. Polymer chain in random coil configuration (Modified from Bolto and Gregory, 2007).

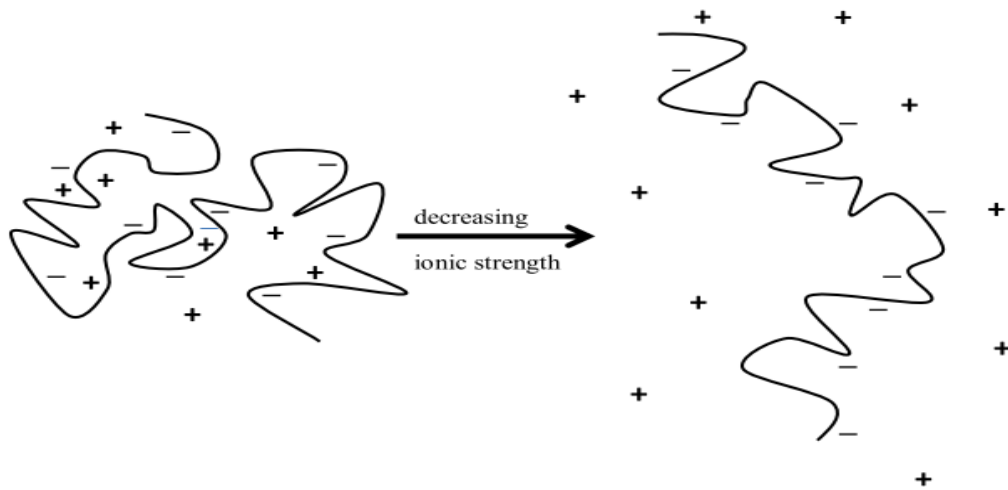


Figure 5. Showing a random polymer coil configuration and the expansion of a poly electrolyte chain with decrease ionic strength (Modified from Bolto and Gregory, 2007).

3.2 Types of polymers

Organic polymers can generally be divided into natural and synthetic polymers. Natural polymers have an advantage that they are; virtually not toxic to humans, environmentally biodegradable and can be readily available to rural communities in the underdeveloped world. The use of natural polymer may be limited because they may not be effective in all cases and their properties cannot be modified. Examples of natural polymers include; chitosan, guar gum, starch, tannin and sodium alginate, Synthetic polymers on the other hand could be toxic to humans but due to the fact that their characteristics (MW and CD) can be easily modified and optimized during the manufacturing process, they are more widely used. Types of organic polymers include cationic, anionic and nonionic polymers. Figure 6 shows common examples of cationic, anionic and nonionic polymers and their chemical structures (Lee et al, 1998; Bratby, 2006 pp 50-56; Bolto and Gregory, 2007).

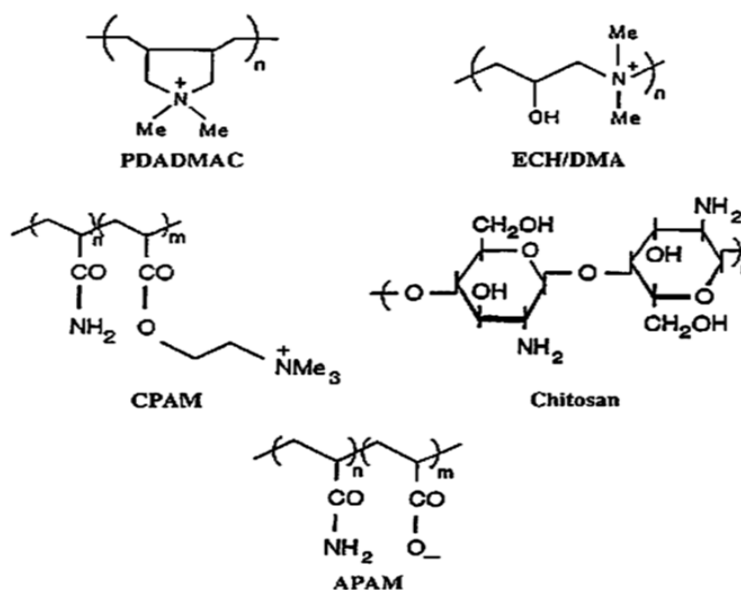


Figure 6. Common structures of cationic (PDADMAC, ECH/DMA, CPAM) and anionic (APAM) synthetic polymers and natural polymer chitosan (Bolto and Gregory, 2007).

3.2.1 Cationic Polymers

These are positively charged polymers commonly used as primary coagulants. Cationic polymers can also be natural or synthetic based. Polydiallyldimethyl ammonium chloride (pDADMAC), Epichlorohydrin/dimethylamine polymers (ECH/DMA) and Cationic Polyacrylamides (CPAMs) are examples of cationic synthetic polymers while Chitosan is an example of cationic natural polymer. PDADMAC and ECH/DMA are water soluble containing about 10 to 50% active polymers with low to medium and medium molecular weights respectively. ECH/DMA is also called polyamines (Bolto and Gregory, 2007; Bratby, 2006 pp. 52-62).

As earlier mentioned one main characteristic of polymers is their charge density (C.D), Table 1 shows a list of commonly used cationic polymers and their C.Ds ranging from 1.2 meq/g CPAM to 7.3meq/g ECH/DMA. Higher charge density or percentage hydrolysis means the polymer has larger loops which will result in more enhanced bridging and more effective destabilization (Bratby, 2006 pp. 195).

Table 1. Charge densities of cationic polyelectrolytes (Bolto and Gregory, 2007).

polymer	Molecular formula	CD (mol%)	CD (meq/g)
PDADMAC	$C_8H_{16}NCl$	100	6.2
ECH/DMA	$C_5H_{12}ONCl$	100	7.3
CPAM	$C_8H_{16}O_2NCl$	100	5.2
CPAM	$(C_8H_{16}O_2NCl)_{0.5}(C_3H_5ON)_{0.5}$	50	3.8
CPAM	$(C_8H_{16}O_2NCl)_{0.25}(C_3H_5ON)_{0.75}$	25	2.5
CPAM	$(C_8H_{16}O_2NCl)_{0.1}(C_3H_5ON)_{0.9}$	10	1.2
Chitosan	$C_6H_{11}O_4N.HCl$	100	5.2

3.2.2 Anionic Polymers

Anionic polymers are ampholytic polymers which acquire a negative charge when the ionizable groups dissociate. Examples of anionic polymers include APAMs (Figure 6), many sulfate polysaccharides (heparin, mannan sulfate, dextran sulfate and chondroitin sulfate) and starch with carboxylic substitutions (Voycheck and Tan, 1993 cited by Bolto and Gregory, 2007; Bolto and George, 2007; Bratby, 2006 pp.54). Table 2 shows the molecular formulas and C.D of some anionic polymers ranging 1.4 meq/g to 10.6 meq/g

Table 2. Charge densities of anionic polyacrylamides (Bolto and Gregory, 2007).

Molecular formula	CD (mol%)	CD (meq/g)
$C_3H_3 O_2Na$	100	10.2
$(C_3H_3 O_2Na)_{0.75}(C_3H_5 ON)_{0.25}$	75	8.5
$(C_3H_3 O_2Na)_{0.50}(C_3H_5 ON)_{0.50}$	50	6.1
$(C_3H_3 O_2Na)_{0.25}(C_3H_5 ON)_{0.75}$	25	3.3
$(C_3H_3 O_2Na)_{0.1}(C_3H_5 ON)_{0.9}$	10	1.4

Another natural polymer that forms a negative charge electrolyte is the non-toxic extract from brown seaweeds called sodium alginate. It is commonly used as flocculant aid in the United Kingdom and Japan (Bratby, 2006 pp. 56).

3.2.3 Non-ionic Polymers

Common non-ionic polymers are; polyacrylamides (PAMs), natural polymers like starch without substitutions, galacto mannans, cellulose derivative, gelatins and glues. Non-ionic polymers vary in structure, molecular weight, and degradability; they are used to aid solid-liquid separations as flocculant. Like most natural polymers their toxic

free nature makes them generally acceptable on health grounds (Lavine, 1981; Rath and Singh, 1997 cited in Bolto and Gregory, 2007; Bratby, 2006 pp. 54-56).

3.3 The use of organic polymers as primary coagulants

Studies carried out by Micheals and Morelos, 1995 cited in Bolto and Gregory, 2007 shows that polyelectrolytes could be successfully used as primary coagulants in water and wastewater treatment.

The use of organic polymers as primary coagulants have a lot of advantages, nevertheless, it can be quite challenging. The most significant of which is the selection of the right polymer to use under the circumstances in question. This involve a look into their molecular weight, charge density, structure, dose, mixing condition, amount and type of impurities found in the water and pH dependency (Ghosh et al., 1985; Bolto et al., 1998; Lurie and Rebhun, 1997 as cited in Bolto and Gregory, 2007; Bratby, 2006 pp. 196). Some advantages of the use of organic polymers as coagulants include; dissolved salt reduction in treated water, less sludge, no metal hydroxide precipitate, less reliance on pH and lower dosage requirement (Bolto and Gregory, 2007).

Polymer usages in water and wastewater treatment also have its drawbacks to the environment, the danger of over or under dosing can be very damaging and could lead to; (Veal 1990 as cited in Bolto and Gregory, 2007)

- high turbidity and color in supernatant water
- re-dispersion of impurities
- increase in sludge formation

There is therefore need to pay attention to the polymer dosage throughout the treatment process. According to Bolto and Gregory (2007) other important issues are;

- polymer toxicity, though less a problem with anionic and non-anionic polymers
- residual polymer analysis in the resultant water

- polymer degradation and
- Disinfection by-product, some cationic polymers like pDADMAC and pAMINE when used properly will produce very insignificant amount of DBPs from chlorine.

Cost of organic polymers could be another drawback but advantages like lower dosages, filter backwash saving, reduced filter loading, increase turbidity removal and reduced sludge could offset the overall cost in favor of organic polymers in the long run. Bratby (2006) stated that “a 5.4h increase in filter run time equated to an 18% reduction in the volume of backwash water required, and a saving of US\$0.12/kl of product water”. He further argued that the lowest cost polymers were not the most cost effective.

3.3.1 Turbidity and suspended solid removal

The optimum dosage requirement for organic polymers will be influenced by the type of material in the raw water, and it is inversely dependent on the size of the particles in suspensions. Where the particle sizes are small with the resultant high surface area more polyelectrolytes are require achieving optimum stabilization, on the other hand a wider optimum dosage range is achieved with larger range particle size. The relationship between particle concentration and pDADMAC dosage was investigated by Black et al., 1965 (cited in Bolto and Gregory, 2007). Their research showed a linear relationship between clay concentration (mg/l) and optimum polymer dosages ($\mu\text{g/l}$), where the clay concentration was doubled the optimum polymer dosage required was as well doubled; at a concentration of 20 mg/l the required optimum polymer dosage was 40 $\mu\text{g/l}$, at clay concentration of 30 mg/l optimum polymer dosage was about 60 $\mu\text{g/l}$ and at 60 mg/l required optimum polymer dosage was 120 $\mu\text{g/l}$.

The dosage requirement for polyamine varies from (1.5 to 9.0 mg/l) depending on the removal of turbidity and color (

Table 3) (Deeble, 1976 cited in Bratby, 2006).

Table 3. Removal of turbidity and color with Pt-Co Deeble (1976) cited in Bratby (2006).

	before treatment	after treatment
Turbidity	5 – 30 mg/l	1 mg/l SiO ₂
Color	30 – 140 mg/l	5 mg/l Pt-Co

According to Nozaic et al (2001 cited in Bratby, 2006 pp. 200) optimum dosage of cationic polymer was much lower than that of alum. This is one of the advantages in the use of organic polymer compared to metal salt coagulants. He also showed that over dosage of cationic polymers can lead to charge reversal; when dosages above optimum of organic polymers were applied, it resulted in charge reversal and an increase in turbidity. This was nevertheless not the case when alum was overdosed.

Greater rates of filtration with better turbidity removal through coarser media is achieved with cationic polymers as oppose to metal coagulant Bratby, 2006 pp. 196-197. ECH/DMA with polymer range of 10,000 and 50,000 Dalton were appropriate for with highly turbid raw water (Lee et al., 2001 as cited in Bolto and Gregory 2007).

3.3.2 Removal of organic matter

Natural organic matter (NOM) is mostly composed of humic substances. NOMs have similar chemical properties but varying physical properties, hence they require different chemical treatments (Bratby, 2006 pp. 88). NOMs cause the majority of the visual problems in most waters (Vaezi et al., 2005; Jian-Jun Qin et al., 2006). Organic polymers with higher MW are most appropriate in treatment of water with NOM according Bolto et al., (1999, cited in Bolto and Gregory, 2007).

Table 4 shows a classification of humic substances into four fractions based on Odens classification.

Table 4. Classification of humic sbstances (Bratby, 2006 pp. 88).

Group Name	Alternative Name	Definition
Humus coal	Humin, ulmin	Insoluble in water and sodium hydroxide
Fulvic acid	Crenic and aprocrenic acids	soluble in sodium hydroxide and mineral acid
Hymatomelanic acid	Hematomelanic, ulmic acids	Soluble in sodium hydroxide and alcohol, insoluble in mineral acids
Humic acid	-	Soluble in sodium hydroxide insoluble in mineral acids and alcohol.

Humic substances in water decrease water quality by; impacting taste to water, blocking lights thereby impeding photosynthesis, transport heavy metals and organic pollutants, and most of all they are repulsive for aesthetic reasons (Bratby, 2006 pp. 88-89).

Color removal besides turbidity is the main prerequisite for a good polyelectrolyte since they vary in their color removal efficiency. The removal percentage ranged from 3 % to 87 % and best performance dosage ranging from 2 mg/l to 16 mg/l for the various tested polyelectrolytes (Packham, 1972 cited in Bratby, 2006 pp. 200).

The coagulation mechanism of organic matter removal is mainly charge neutralization; there is evidence of a correlation between best dosage and charge neutralization. The

cationic charge of the polyelectrolyte can be stoichiometrically related to the anionic charge of the humic particles making the charge density mostly responsible in eliminating humic materials (Bolto et al., 1999; Kan and Gregory, 2001 cited in Bolto and Gregory 2007; Bratby, 2006).

Higher charged polymers require less dosage for optimum results than lower charged polymers. Highly charged cationic polyelectrolytes generally are most appropriate in municipal wastewater treatment and are quite good in total suspended solids (TSS) and chemical oxygen demand (COD) elimination from wastewaters with a purification efficiency of about 84 % to 98 % but less appropriate in phosphorous removal (Bratby, 2006 pp. 203-204).

4 Research Methods and Materials

The objective of this research was to evaluate the suitability of organic polymers as coagulants and flocculants agents for the purification of peat extraction runoff water. The aim was to test under laboratory conditions the purification efficiency achieved by selected organic coagulants and compare their performance with the metal salt coagulant ferric sulphate (PIX 115 – Kemira Oyj, Kemwater). Furthermore, to identify the required coagulants dosages, mixing requirements and sedimentation characteristics. The influence of temperature and pH in purification efficiency, and sedimentation characteristics of tested coagulants were also evaluated.

About 500 litres of water was collected from the ditches of the Kurkisuo peat extraction site prior to chemical treatment. The samples were kept in pre-acid washed galloons and stored in a cold room (5 to 10⁰ C). Water quality analyses (Table 5) were performed in each of the used gallons (total of 12) so that information of initial water conditions and variations in water quality during storage were determined. The average water quality of Kurkisuo samples is shown in Table 6.

Table 5. Water quality performed and utilized standard methods.

Analysis	Abbreviation's	Standard
Total organic carbon	TOC	SFS-EN 1484:1997
Total nitrogen	T.N	SFS-EN ISO 11905-1:1998
Total Phosphorous	T.P	In-house method 51b,FIA method
Phosphate phosphorous	PO ₄ -P	In-house method 55b,FIA method
Suspended solids	SS	SFS-EN 872:2005

Table 6. Kurkisu water quality (n = 12).

Parameters	Average water quality	Standard deviation
T.N ($\mu\text{g/l}$)	2200.0	405.0
T.P ($\mu\text{g/l}$)	74.7	4.6
PO ₄	44.2	5.9
SS (mg/l)	20.8	5.2
TOC (mg/l)	30.7	0.9
Fe ($\mu\text{g/l}$)	6745.5	486.5
Al ($\mu\text{g/l}$)	862.9	261.5
Turbidity (NTU)	50.5	4.9
Color mg Pt/l	396.4	12.1

4.1 Selected chemicals

The organic polymers being tested (Table 7) were selected based on required characteristics such as molecular weight and electric charge. The pre-hydrolyzed metal salt coagulant ferric sulphate (PIX 115) was selected because it is the coagulant now used at Kurkisu treatment facility and for which optimization of process parameters are required.

Table 7. Characteristics of tested chemicals.

Brand name	Chemical type	Characteristics	Manufacturer	Density g/cm ³
Coagulant Superfloc C-587	Polydiallyldimethylammoniumchloride (PolyDADMAC)	Liquid Medium molecular weight and high relative cationic charge	Kemira Oyj, Kemwater	1.03-1.05
Coagulant Superfloc C-567	Epichlorohydrin-copolymer (PolyAMINE)	Liquid Low molecular weight and high relative cationic charge	Kemira Oyj, Kemwater	1.14-1.18
Coagulant PIX-115	Pre-hydrolysed Metal salt coagulant (PolyFerric sulphate)	Liquid	Kemira Oyj, Kemwater	155

4.1.1 Preparation and handling of selected coagulants

Stock solutions of 10 mg/l of selected coagulant were prepared in a 200 ml flat bottom flask. Dilutions were prepared using equations (3) and the density of the individual coagulants (Table 7).

$$C_1V_1=C_2V_2 \quad (3)$$

Where;

C_1 = initial concentration,

C_2 = final concentration,

V_1 = initial volume and

V_2 = final volume

As the density of polyamine (pAMINE) is 1.16 g/cm^3 or 1160 mg/ml , from equation 3 the volume require to make a solution containing 10 mg/l of the product pAMINE in the 200 ml flask was calculated to be 1.724 ml , similar procedure was applied in the preparation of stock solutions of polyDADMAC (pDADAMAC) (1.920 ml) and PFS (1.290 ml). The prepared coagulant solutions were stored at room temperature and used for up to 3 days after which they were discarded and a new solution prepared.

4.2 Laboratory tests

Jar test equipment were used to carry out the experiment and on the spot analysis like turbidity, color, pH and electric conductivity were performed and recorded, further analysis were carried out by SYKE certified laboratory.

Before starting each experiment, the galloon to be analyzed at each stage is vigorously shaken, this allowed for in-depth mixing to prevent water quality changes caused by settling. The laboratory experiments were carried out in the following stages:

1. Dosage optimization and determination of purification efficiency at $22 \pm 1 \text{ }^\circ\text{C}$,
2. Mixing optimization,
3. Settling characteristics,
4. Dosage optimization and determination of purification efficiency at $2 \pm 2 \text{ }^\circ\text{C}$,
5. Influence of temperature and pH adjustment.

Stage 1 required 12 jar tests, stage 2 which is mixing parameter optimization 8 jar tests were required, 9 jar tests were required in stage 3. Stage 4 which is dosage optimization and determination of purification efficiency at low temperatures required 3 sets of jar tests which were done as follows; 3 dosages, 2 replica for the 3 coagulants. Each set of jar required on the spot test of turbidity, color, pH, and conductivity. These stages required 2300 litters of raw water for total of 38 jar tests with 24 sets of supernatant waters sent for further analyses.

Jar tests

The apparatus consist of six one liter jars containing six peddles (Figure) which can rotate at various speeds and time adjusted by the flocculator device in Figure 8. The dimension of the individual jars and stirrers used in the in the jar test apparatus are listed in Table 8.



Figure 8. Jar test apparatus used in this study (Photo by Joseph Ngakfumbe, 2012).

Table 8. The dimension of the individual jars and stirrers.

Beaker	Dimension	Stirrers	Dimension
Height	18 cm	Length	15 cm
diameter	9 cm	Width of paddles	3 cm
Volume	1 l	Length of paddles	5.6 cm

Jar test procedure;

- Fill in each of the individual jars with 1 liter of water sample.
- Apply constant and equal mixing parameters as well as sedimentation time to all the jars. Constant mixing parameters applied: Fast mix speed: 300 rpm; fast mix time: 10 sec; Slow mix speed: 50 rpm; Slow mix time: 25 min. The speeds and times were adjusted using the flocculator 200 Figure 9. Sedimentation time of 30 min was applied.

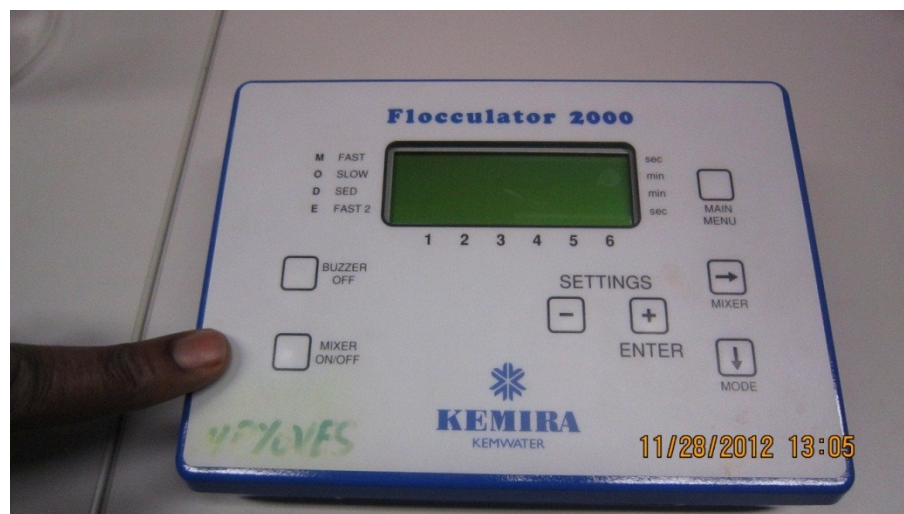


Figure 9. Flocculator 200 used in varying flocculation speeds and times (Photo by Joseph Ngakfombe 2012).

- Add incremental dosages of the coagulant from jar 1 to jar 6 and start the running the experiment.
- Supernatant water was carefully extracted from each jar soon after sedimentation time and analyzed on the spot for turbidity, color, pH and conductivity.
Purification efficiency of each jar was evaluated and expressed in the ratio of; turbidity of the treated water (T) against turbidity of the raw water (T_i), and color of the treated water (C), against color of the raw water (C_i). The turbidity and color were measured using the HACH Ratio XR turbidity meter and Lovibond color measuring device Figure 10 and
- Figure respectively.



Figure 10. Turbidity meter used for measuring turbidity (Photo by Joseph Ngakfombe 2012).



Figure 11. Lovibond device used in measuring color (Photo by Joseph Ngakfombe 2012).

- About 400 ml of supernatant water is carefully extracted from the jar which presented the best removal of color and turbidity after a total of 45 minutes of sedimentation. The extracted samples was then sent for further analyses.

Stage 1 – Jar test procedure

Three replication of the jar test procedure was performed in this stage of laboratory experiments where increasing dosages of the individual coagulants were applied into the 6 sequential jars. The best or the optimum dosage was sent for further analysis from each replica. With pAMINE a dosage range of 20 mg/l to 80 mg/l was applied while a range from 50 mg/l to 110 mg/l was applied for pDADMAC, and dosages from 120 mg/l to 220 mg/l were tested for PFS. The mixing parameters were constant for all the experiments as detailed in the previous section.

Stage 2 - Optimization of mixing

Using the one factor at a time procedure a series of jar tests were carried out to investigate the influence of each mixing parameters on the purification efficiencies of each of the chemicals. Mixing speeds and times were investigated while the settling time stayed constant at 30 minutes in all the experiments.

The experiments were carried out as follows;

- Three jars were filled with raw water and dosed with the optimum dosage of the coagulant in question (50 mg/l, 80 mg/l and 200 mg/l for pAMINE, pDADMAC, PFS respectively).
- The stirrers of each of the three jars were programed with one of the four mixing parameters different in each of the jars and the other three remaining constant as shown in .

➤ Table 9.

Table 9. Fast mixing times and speeds.

Fast mixing		Slow mixing	
Time (seconds)	Speed (rpm)	Time (minutes)	Speed (rpm)
10	100	5	20
30	200	10	50
60	300	15	70
90	400	25	90

Stage 3 – Settling

The settling characteristics of the coagulants were investigated in two experiment replications for each chemical at room and low temperatures; jar test procedure was followed with the following modifications;

- The jars marked at 8cm from the bottom.
- The optimum dosage of the coagulant to be investigated was then added, a sample is collect from jar a minute before the end of slow mixing time and 10 other samples are collected at 1, 2, 3, 4, 6, 8, 11, 13, 17 and 25 minutes after slow mixing (flocculation) time or during sedimentation.

Stage 4- Influence of low Temperature

Experiments to evaluate the influence of temperatures were performed using a temperature control water tank. The jars containing raw water were placed in the tank until the required temperature of $2\pm 2^{\circ}\text{C}$ was achieved. The optimum dosage at low temperature was tested following the steps in stage 1.

Samples extracted from the jars treated with the optimum dosage of each coagulant were sent for further analyses.

Stage 5- influence of pH

The initial pH of water samples was decreased from 6.5 to 5.5 and then to 4.5 using stock solution of sulphuric acid 0.5 M. When the desired pH was achieved the adjusted raw water samples were then submitted to the procedures highlighted in stage 1 for the evaluation of dosage requirements and purification efficiency, the effect of pH on the settling characteristics were not investigated.

After every step in the jar test procedure the results were recorded in a log sheet. The ratio of treated turbidity (T) and color (C) against turbidity (T_i) and color (C_i) of the raw water were also calculated for each dosage to determine dosage requirement and purification efficiency. Average percentage removal of turbidity and color were also calculated. Similar calculation were done on result from accredited laboratory SYKE results where percentage removal of total nitrogen (T.N), total phosphorous (T.P), phosphate (PO_4), Suspended Solids (SS), total organic carbon (TOC), iron and aluminum. For easy evaluation and visualization graphs were drawn and some cases the results were presented in tables.

5 Results and Discussions

5.1 The determination of dosage requirement and purification efficiency

The results of the determination of dosage requirement and purification efficiency were presented in graph of the ratio of C/C_i and T/T_i against dosage (mg/l). The graph of pH and dosage was also plotted for all tested coagulant at room temperature (22 ± 1 °C) and low temperature (2 ± 2 °C). The average removal of the analyzed substances which shows how they are reduced by each coagulant compared to their initial concentration was also presented at both temperatures.

5.1.1 Optimum dosage and purification efficiency at 22 ± 1 °C

Increasing the dosage of coagulants resulted in an increase in the removal of color and turbidity for all tested coagulants (Figure 12). The dosage requirement of tested coagulant, however, differed considerably; PSF required higher dosage than the pAMINE and the pDADMAC to achieve similar purification levels. The optimum dosage range for pAMINE was found to be from 40 mg/l to 80 mg/l (Figure 12a). There is a sharp drop in turbidity between 20 mg/l and 40 mg/l. The removal of turbidity

peaked at 40 mg/l and further increase in dosage showed little or no change in the removal of turbidity. The optimum dosage for pAMINE was identified as 50 mg/l.

PDADMAC showed slightly different trends of turbidity and color removal compared to pAMINE and the dosage requirements were also higher (Figure 12b), pDADMACs curves presents a gentle slope from 0 mg/l up to about 55 mg/l where there is sharp drop in turbidity when the dosage of 60 mg/l is applied. The best removal was achieved around the dosage of 75 mg/l. As with pAMINE there is no further change in turbidity removal after the optimum dosage was achieved. The pH was also plotted against dosage. For both organic polymers dosage had no effect on the initial pH.

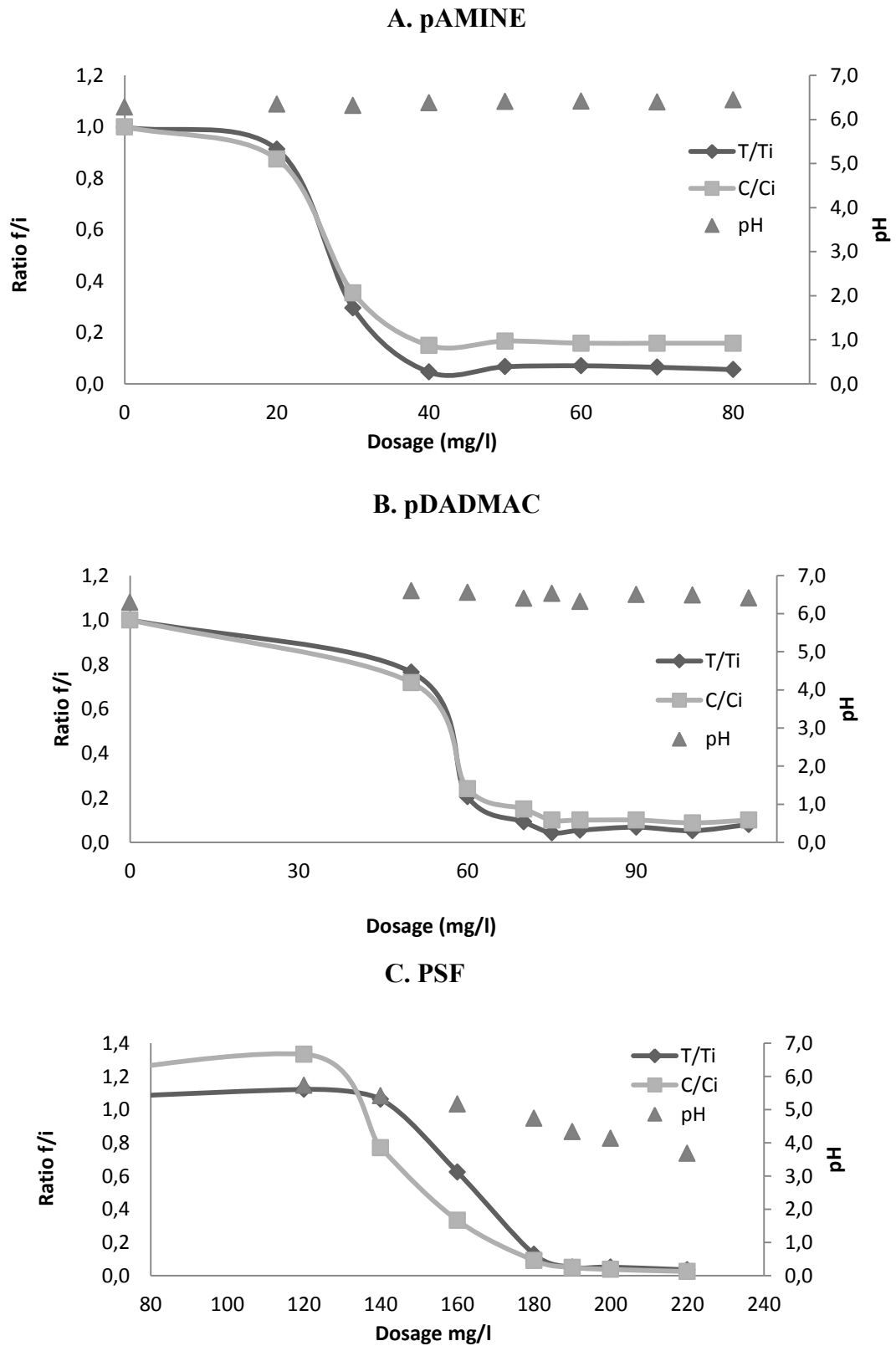


Figure 12. Optimum dosage range determination; removal of color and turbidity with increasing dosage of coagulants.

The optimum dosage for the inorganic coagulant PFS ranged between 180 mg/l – 220 mg/l (Figure 12c). Analysis of obtained results for PFS showed a slight increase in turbidity between 0 to 120 mg/l followed by a relatively gentle drop in turbidity and color between 120 mg/l and 180 mg/l. There was no further change in turbidity removal up to 220 mg/l. The pH was again plotted against dosage and unlike the organic coagulants there was a considerable drop in pH when increasing dosages of PFS were applied from 6.0 to 3.8 at 220 mg/l. The identified optimum dosages for all tested coagulants were; 200 mg/l for PFS, 50 mg/l for pAMINE and 80 mg/l pDADMAC.

The observed average removals T.N, T.P, PO₄, SS, turbidity, color, Fe and Al are presented in Figure 13. The removal of T.P, PO₄, SS, Fe and Al ranged from 80 to 97 %, PFS performed better in the removal of most analyzed substances, and the organic coagulant removed higher amounts of Fe. Samples treated with pAMINE presented more than 40 % increase in their nitrogen content while PFS and pDADMAC remove around 40 % of the initial nitrogen concentration. Low TOC removal was observed with organic polymers, pAMINE removes about 20 %, pDADAMAC around 40 % while PFS removed about 75 %. Where optimum dosages were applied all coagulants achieved high removal of turbidity and color (85-95 %). PFS showed a slightly higher removal of color and turbidity (95 %) compared to the organic coagulants (85-95 %).

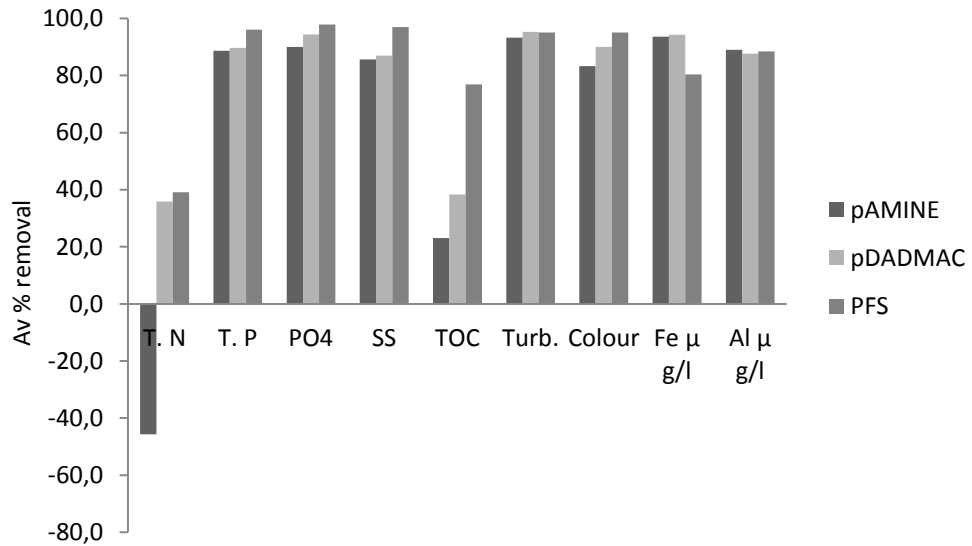


Figure 13. Average removal efficiency of analyzed substances compared with their initial concentration at $22\pm 1^{\circ}\text{C}$.

5.1.2 Purification efficiency at $2\pm 2^{\circ}\text{C}$

During the evaluation of dosage requirements at low temperature for all coagulants it was observed that although the identified optimum dosages were the same as those identified at $22\pm 1^{\circ}\text{C}$ the curves representing the removal of color and turbidity with increasing dosages were slightly different Figure 14. The pH remained unchanged with the organic polymers but decreased steadily with increase in dosage with PFS as is the case at temperature $22\pm 1^{\circ}\text{C}$.

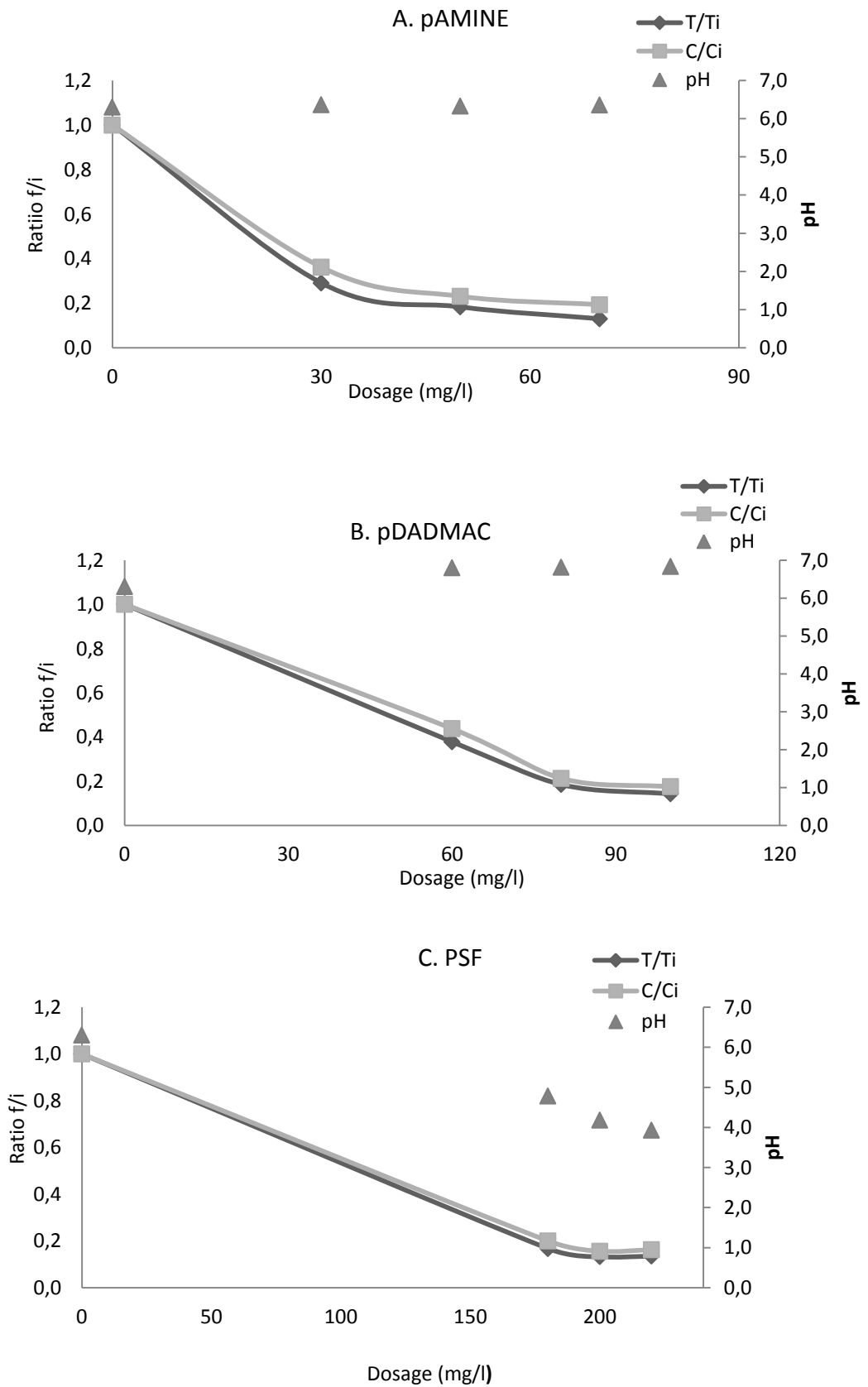


Figure 14. Determination of dosage requirement according to turbidity and color removal for all tested coagulants at 2 ± 2 °C.

In Figure 14a at 30 mg/l for example the results show that pAMINE's removal ratio of color and turbidity was less than 0.4, this is similar to the removal of color and turbidity at room temperature. The impact of low temperature was visible when dosage was above 30 mg/l. In Figure 14b at 60 mg/l pAMINE removed around 60 % of turbidity at low temperatures; it had performed better at 60 mg/l at room temperature removing about 80 % of turbidity. In Figure 14c, 170 mg/l of PFS at 2 ± 2 °C removed about 80 % of turbidity and color; its removal ratio improved only slightly when dosage was increased to 220 mg/l. Although at 22 ± 1 °C and low temperature PFS had a similar percentage removal at 170 mg/l; the removal of turbidity and color improved to more than 95 % at 190 mg/l and above at 22 ± 1 °C.

Comparing the performance of coagulants in the removal of analyzed substances at 2 ± 2 °C (Figure 15), it can be seen that pAMINE did not leach nitrogen into the system rather it removed over 10 %. Furthermore, the removal of T.N was higher at lower temperatures for all tested coagulants. The removal of PO_4 showed no dependence on temperature with pAMINE while with pDADMAC there was a slight decrease in the removal of PO_4 at lower temperatures (Figure 15a). There was a more significant difference in PO_4 removal when PFS was applied, PO_4 removal varied from about 90 % at low temperature to 98 % at 22 ± 1 °C. The removal of TOC was not very temperature dependent although all tested coagulants performed slightly better at lower temperatures. Total phosphorous removal was also not temperature dependent; the percentage removal variations were minimal although there was slightly higher removal at 22 ± 1 °C. Nevertheless the removal of SS, turbidity and nitrogen did suffer detrimental effects due to the low temperature applied (Figure 15).

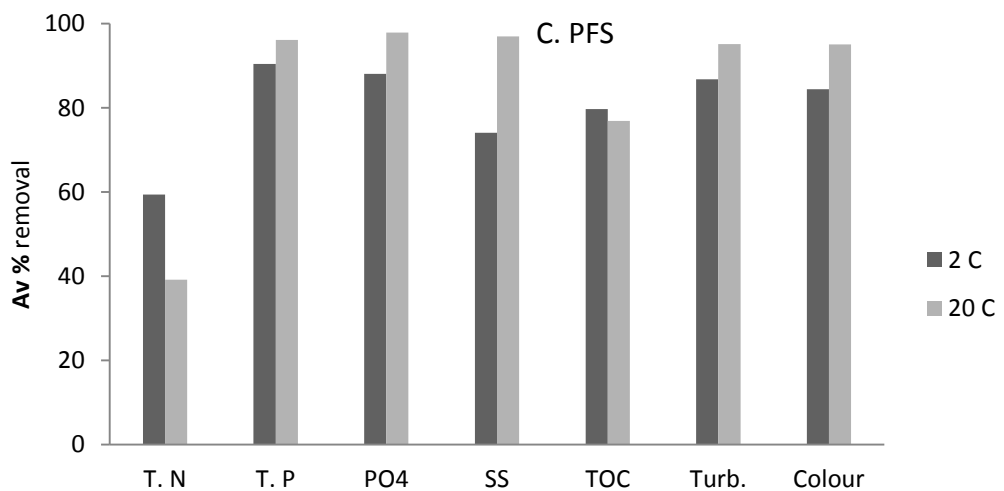
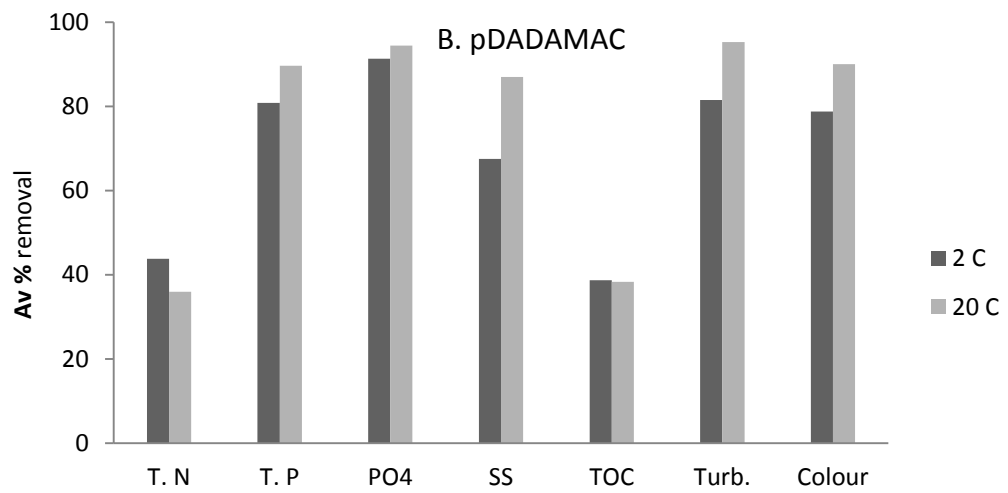
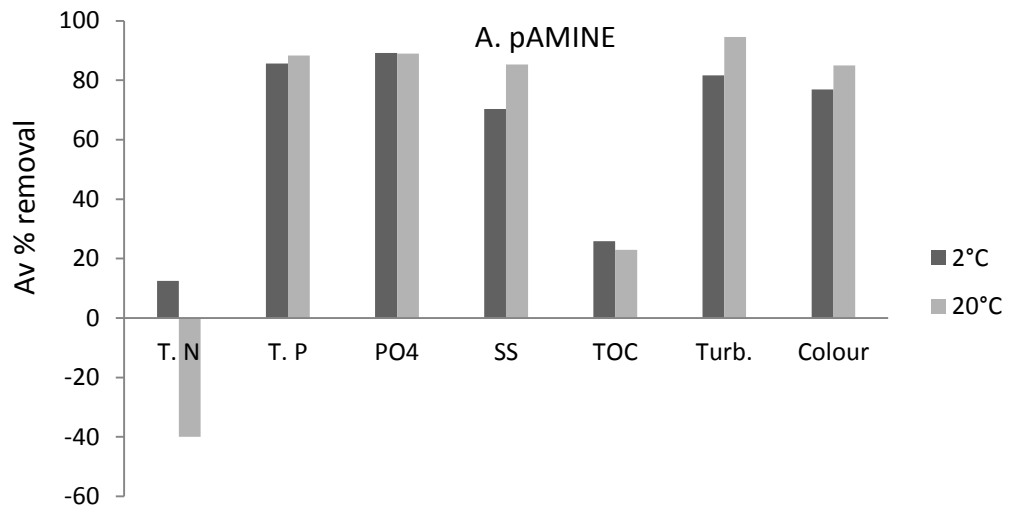


Figure 15. Comparison between removal efficiencies at 2 ± 2 °C and 22 ± 1 °C.

5.1.3 Settling characteristics of tested coagulants.

Settling characteristics is a measure of how flocs generated by the addition of coagulant settle under the applied process parameters.

At $22\pm 1^{\circ}\text{C}$ the settling characteristics of pAMINE and pDADMAC show similar trends when their optimum dosages was applied, the settling begins as soon as slow mixing was completed and hits the 0.2 Tt/Ti ratios or 80 % removal after about 13 minutes. PSF showed slightly better settling characteristics, it achieved the 0.2 ratio much earlier after about 11 minutes.

The settling characteristics were also investigated at low temperatures, the results obtained shows that the coagulants settling rate dropped slightly although similar results were obtained at the end of the 25 minutes settling time. Comparing the settling performance of the tested coagulants at $2\pm 2^{\circ}\text{C}$ and $22\pm 1^{\circ}\text{C}$ Figure 16a, b and c clearly show better settling at higher temperatures. At room temperature all the tested coagulants had their best clarification over 15 minutes of sedimentation but best clarification levels was only achieved close to 25 minutes of sedimentation at low temperature, especially for organic coagulants.

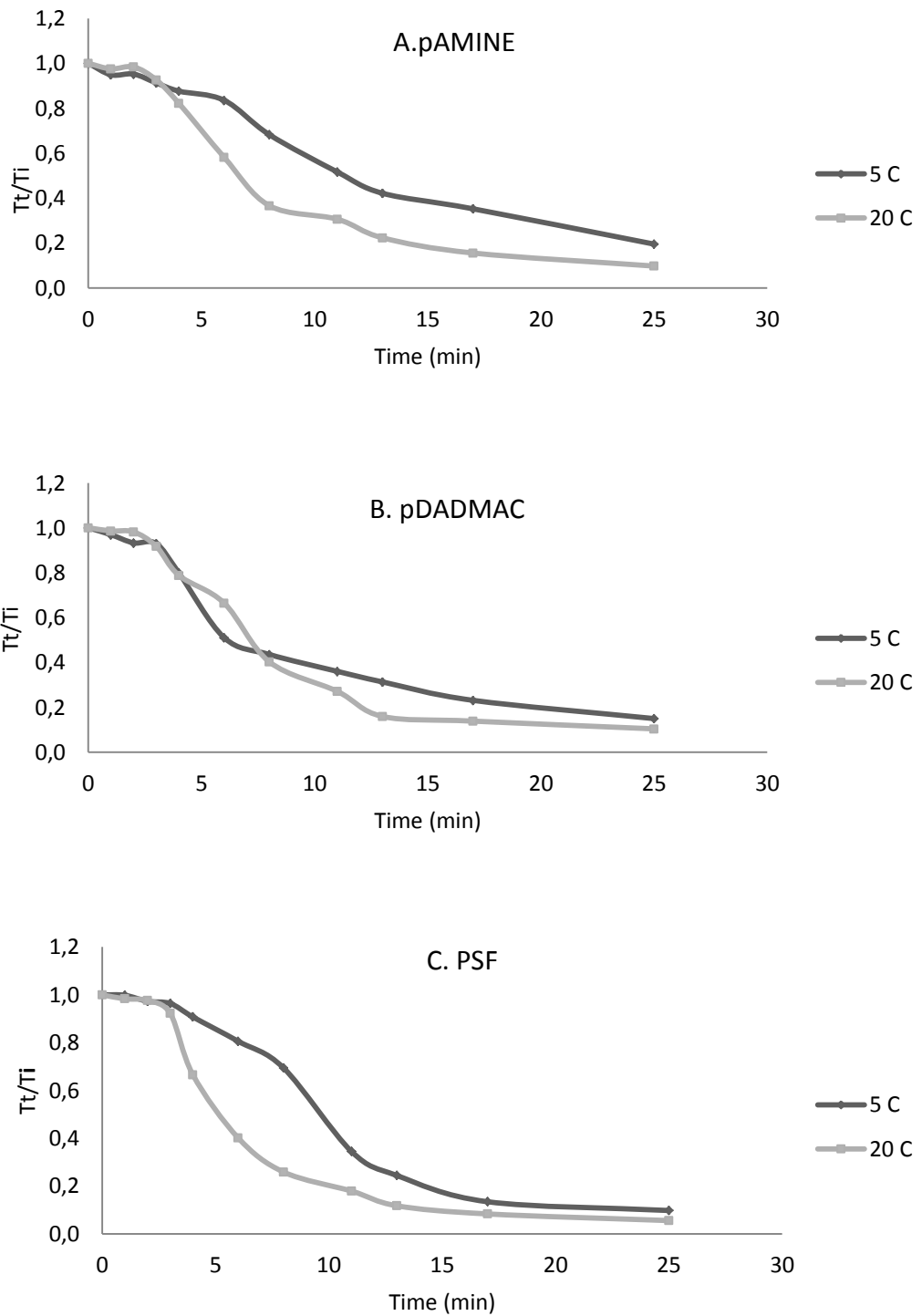


Figure 16. Settling characteristics of tested coagulants at $22 \pm 1^\circ\text{C}$ and $2 \pm 2^\circ\text{C}$.

From Figure 16a pAMINE settled 50 % of particles within the first 7 minutes, while it took approximately 12 minutes at low temperature to settle 50 % of the particles,

pDADMAC showed little variation with change in temperature while PFS reached the 50 % mark within the first 5 minutes at $22\pm 1^{\circ}\text{C}$ but double that time to settle 50 % of flocs at low temperatures.

5.1.4 The determination of dosage requirement and purification efficiency - Discussion

In this study the dosage requirement of the organic coagulant obtained were 50 mg/l to 80 mg/l and 70 mg/l to 110 mg/l for pAMINE and pDADMAC respectively while the dosage requirement for PFS was observed between 170 mg/l to 220 mg/l. This tie with Bratby, 2006 and Nozaic et al 2001 who affirm that, one of the advantages of organic polymers is the lower dosage requirement compared to inorganic coagulants. The purification efficiencies achieved by all tested coagulants varied with the various water quality parameters but most of them were within the projected level for chemical treatment of peat - derived runoff water; 30 - 90 % SS, 30 - 60% T.N, and 75 - 95 % T.P (IPS, 2009, cited in Heiderscheidt et al 2013). For example pAMINE and pDADMAC removed above 85 % SS and T.P, while pDADMAC removed about 38 % of T.N well within expected level of for chemical treatment of peat – derived runoff water. These performances are in line with studies carried out by Micheal and Morelos, 1995 cited in Bolto and Gregory, 2007 affirming that polyelectrolytes could be successfully used as primary coagulants in water and wastewater treatment. Studies carried out by Volk et al, 2000; Matilainen et al, 2005, 2010 cited in Heiderscheidt, 2013, shows the use of iron salts as coagulant favors the removal organic matter, there was therefore comparatively low removal of TOC by the organic coagulants 23 % and 38 % for pAMINE and pDADAMAC respectively compared to 75 % by PFS. There was a slightly higher removal of Fe by the organic coagulants compared to PFS, this again tie with the one the advantages of organic coagulant; reduced dissolved salt in treated water as compared to inorganic coagulants. Where optimum dosages were applied all tested coagulants achieved above 80 % removal within the first 15 minutes. Contrary to Nozaic et al 2001 cited in Bratby, 2006 there was no charge reversal and increase in turbidity when organic coagulants were applied beyond optimum dosage, there was steady increase in removal of turbidity with increases in dosage.

Low temperatures will slowdown reaction rate and increase viscosity (Yu et al, 2006). Our results clearly portray lower removal efficiency in most of the parameters at low temperatures; 18 % reduction in SS, 16 % drop in removal of turbidity, 11 % drop in color with pAMINE, and 24 % drop in SS, 11 % reduction in turbidity, 11 % drop in color with pDADMAC when temperatures were lowered. Similarly reduced performances were also observed with PFS; 26 % reduction in SS and 0.5 % reduction in turbidity and color. However, all tested coagulants showed little or change in removal of TOC, T.P, and PO₄ at lower temperatures while there was an increase in the percentage removal of T.N with all tested coagulants.

5.2 Optimization of mixing parameters

The goal of optimizing the mixing parameter was to establish the effects of the different stages of mixing on purification efficiency as well as to identify the most optimum mixing parameters for the individual coagulants. Various mixing speeds and different times were investigated. The results for mixing optimization are present based on turbidity removal.

5.2.1 Coagulation or fast mixing stage

Figure 17 shows the effects of fast mixing speed and time variation on percentage removal of turbidity. The slow mixing speed and time were 50 rpm and 25 minutes respectively; the result show that fast mixing had less effect on organic coagulant, at 0 rpm or when there was no fast mixing pAMINEs removal of turbidity was above 80 % and pDADMAC about 70 %. According to the results PSF is much more dependent on fast mixing; its removal efficiency of turbidity when no fast mixing was applied was only about 20 %. The removal efficiency improved significantly when fast mixing was applied. The percentage removal of the organic polymers improved with increase in speed and peaked at 300 rpm while PFS removal did not vary beyond 100 rpm with increase in mixing speed. The best fast mixing speed was 300 rpm for the organic polymers and it ranged from 100 rpm to 400 rpm for PFS. There was a slight reduction in percentage removal of turbidity beyond 300 rpm for the organic coagulants.

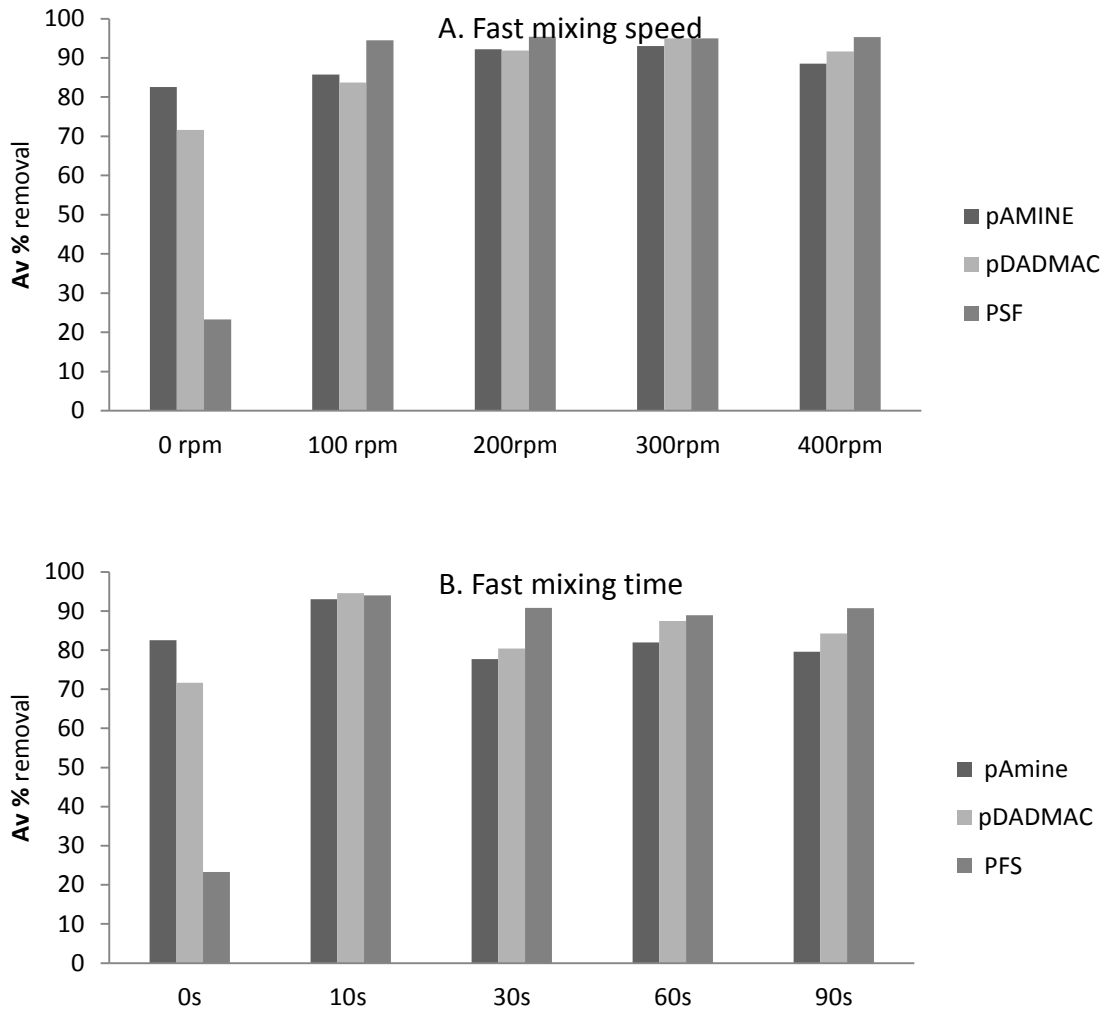


Figure 17. The effects of fast mixing speed and time on percentage removal of turbidity.

With fast mixing time fluctuating from 0 s up to 90 s all three tested coagulant peaked at 10 s, there was a general fluctuation in percentage removal between 10 s and 90 s. As was the case with fast mixing speed, PFS's performance was relative weak at 0 s mixing time. The best fasting mixing time was found to be 10 s for all coagulants. The performance of PFS did not change much with longer mixing times beyond 10 s but there a drop in the performance of the organic coagulants though it was stable between 30 s and 90 s.

5.2.2 Flocculation or slow mixing stage

During this phase fast mixing speeds and times were fixed at 300 rpm and 10 s respectively. At 0 rpm or no slow mixing all tested coagulants presented low removal efficiency, pAMINE suffered least with a percentage removal of turbidity of about 42 %, PFS about 33 % while pDADMAC suffered most. When no slow mixing was applied pDADMAC increased the sample initial turbidity increasing turbidity by 20 %. With slow mixing speed percentage removal peaked at 20 rpm for all the tested coagulant. There was no significant change in the performance of the coagulants when the speed was increased above 20 rpm, there was a slight drop though in the performance of organic coagulants at higher speeds reducing from 90 % to 82 % with pAMINE, and about 92 % to 85 % with pDADAMAC between 70 rpm and 90 rpm (Figure 18). The best slow mixing speed for all tested coagulant was found to be between 20 to 50 rpm.

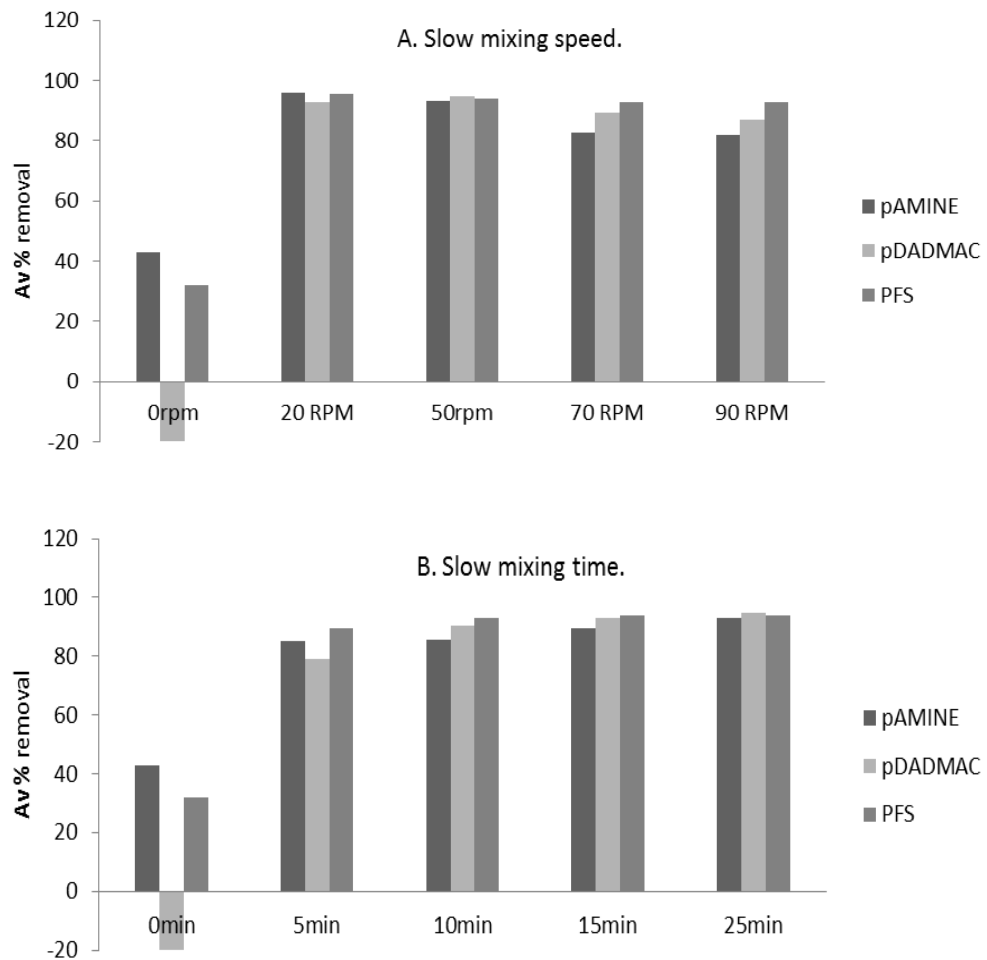


Figure 18, - The effects of slow mixing speed and time variation on percentage removal of turbidity.

Regarding the influence of slow mixing time, a sharp surge is observed in percentage removal of turbidity when slow mixing time was applied (5 minutes) for all tested coagulants. The removal of turbidity increased progressively up to the 25 minutes mark. All tested coagulants showed a similar pattern with slow mixing speed although pDADMAC was relatively weaker at mixing times less than 10 minutes (Figure 18).

5.2.3 Influence of mixing - Discussion

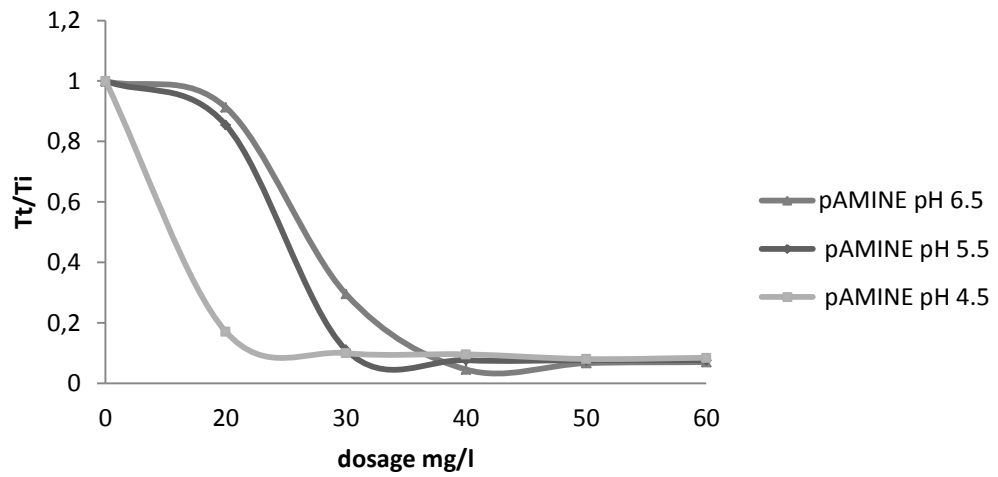
Our results show that the tested organic coagulants were not significantly affected by variations in fast mixing speed. At 0 rpm pAMINE had a percentage removal of turbidity above 80 % and pDADMAC above 70 % while PFS above 20 %. This is in line with earlier studies carried out by Heiderscheidt et al., 2013; Rossini et al., 1998; Kan et al., 2001. Working with metal salts they found a strong reliance of their performance on rapid mixing. When no slow mixing was applied, all coagulant's performances were relatively poor; pDADMAC suffered the most and presented a 20 % surge in turbidity. The other coagulants pAMINE and PFS removed around 40 % and 35 % respectively. Nevertheless all coagulant soon peaked between 20 rpm and 50 rpm.

5.3 Influence of pH on purification efficiency

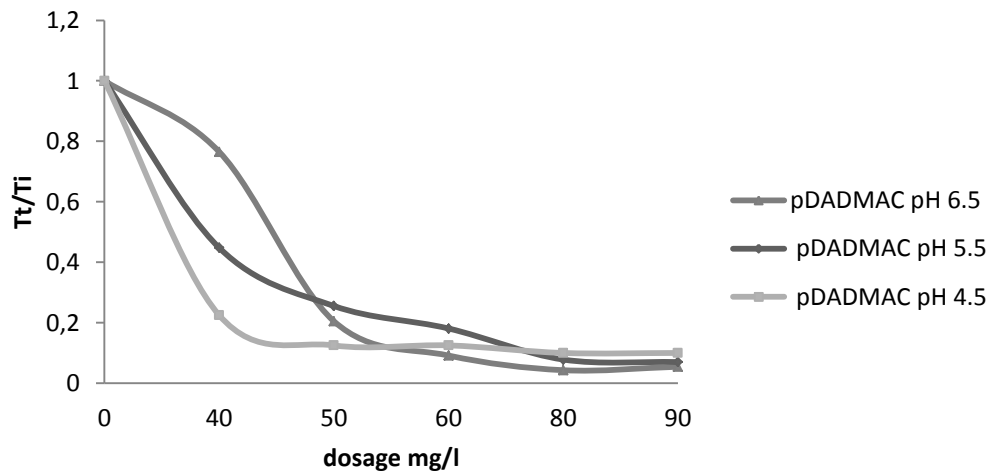
The influence of pH on the purification efficiencies was tested and the results are shown in Figure 19a, b and c. In comparing the obtained results for pAMINE at 20 mg/l it is clear that dosage requirement decrease with decreasing pH. For pH 4.5 pAMINE had already achieved a removal of turbidity of above 80% while at pH 5.5 the removal was only about 20% at the same dosage. The coagulant had similar removal efficiency at both pH 4.5 and 5.5 after 30 mg/l (Figure a). The optimum dosage was identified as 30 mg/l and 40 mg/l for pH 4.5 and 5.5 respectively. Figure b shows that similar conditions were observed for pDADMAC, at 40 mg/l pDADMAC had achieved a removal percentage of less than 60% while at pH 4.5 the dosage of 40 mg/l had achieved about 80% removal.

According to the obtained results the performance of the inorganic polymer PFS was the most dependent on pH. PFS dosage requirements greatly reduced with lower pH. At pH 4.5, a dosage of 120 mg/l of PFS had already achieved best removal of more than 85 % while at the same dosage it removed barely 50 % of turbidity at pH 5.5 (Figure 22c).

A. pAMINE



B. pDADMAC



C. PFS

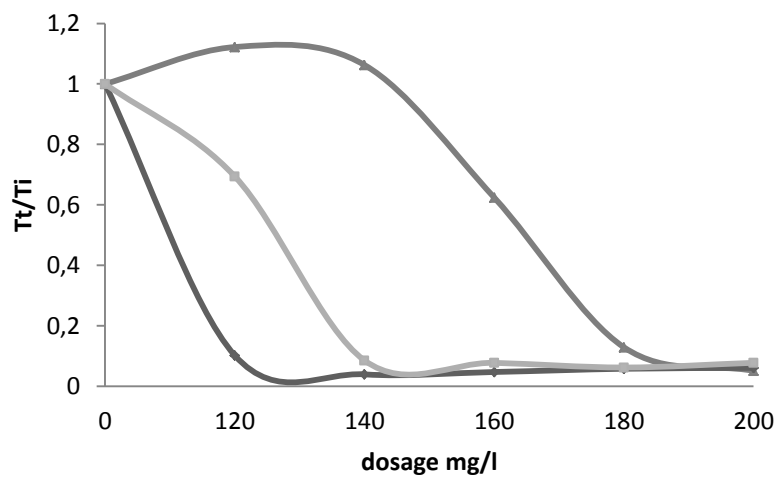


Figure 19. Removal of turbidity with increasing dosages at pH 4.5 and 5.5.

The surge in turbidity when PFS was added at pH 6.5 was not observed in the experiments with lower pH values. The purification efficiency achieved by the identified optimum dosages at different pH is presented in Figure 20 and 21. At pH 5.5 there was again leaching of T.N observed when pAMINE was used, although there was a slight drop in the percentage of T.N leached. At pH 6.5 pAMINE leached about 43 % of T.N while at 5.5 the leaching was reduced to about 20 %. TOC removal improved slightly from 25 % at pH 6.5 up to 30 % at pH 5.5. T.P, PO₄, SS, and Al were not pH dependent showing similar removal efficiencies at different pH levels. At pH 5.5 PFS struggled with the removal of Fe, dropping from 80 % at pH 6.5 to less than 30 % at pH 5.5.

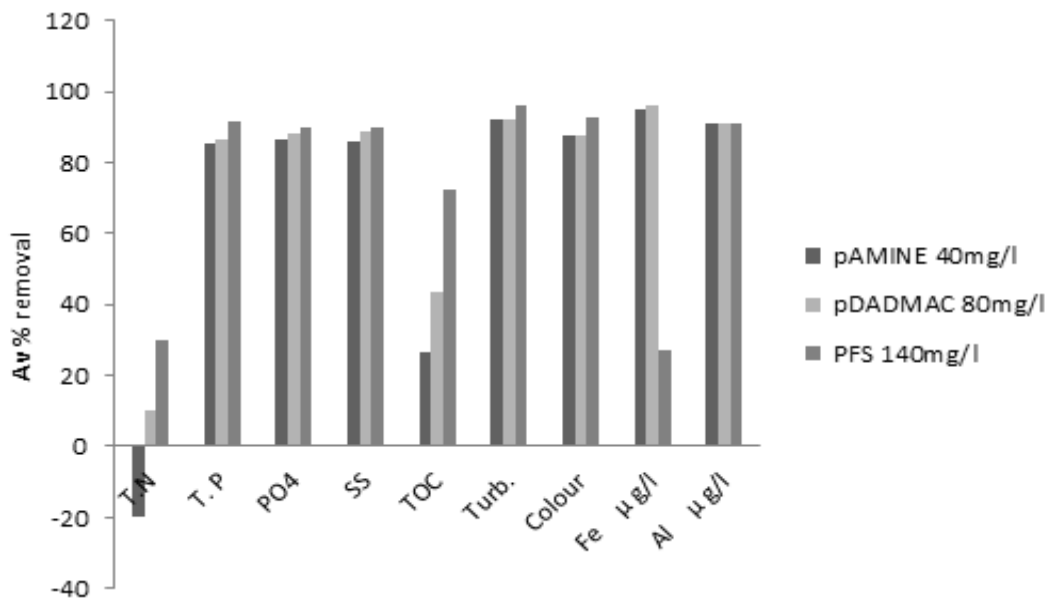


Figure 20. Comparison of the purification efficiency achieved by tested coagulants at pH 5.5.

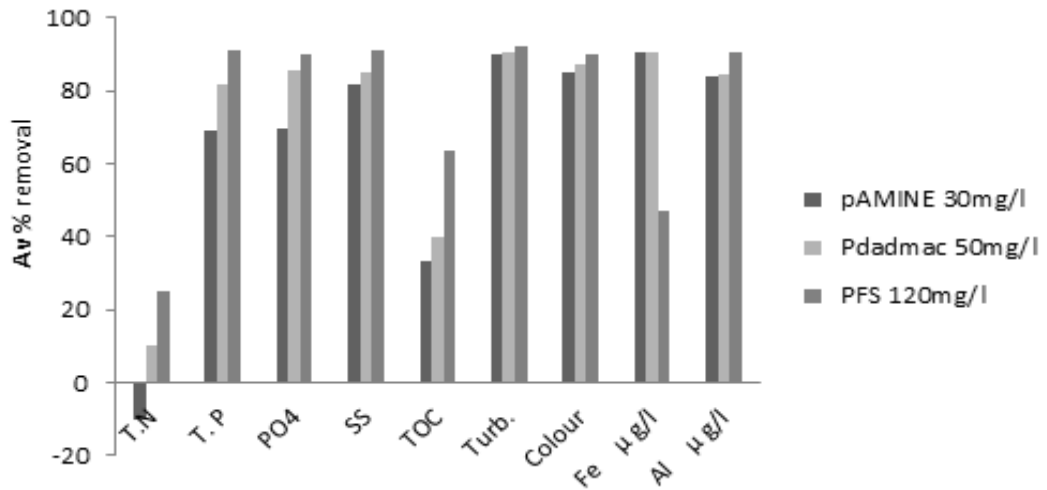


Figure 21. Comparison of the purification efficiency achieved by tested coagulants at pH 4.5.

There was again leaching of T.N into the system with pAMINE at both pH of 4.5 and 5.5, though there was a slight reduction in amount of Fe leached as pH decreased from 43 % at pH 6.5 (Figure 13), down to 20 % and 10 % at pH 5.5 and 4.5 respectively. There was an improvement in removal of TOC with pAMINE from 22 % at pH 6.5 up to about 38 % at pH 4.5. PSF showed a visible drop in the removal of Fe from about 80 % at pH 6.5 down to 30 % and 42 % removal at pH 5.5 and 4.5 respectively, PFS showed an improved performance in the removal of Al from less than 80 % at pH 6.5 to more 90 % at pH 4.5.

Where optimum dosages were applied at the various pH levels, the removal efficiency was 90% and above Figure 22. Although lower pH values had lower optimum dosage requirements, they all had an average removal of turbidity of more than 93 % at pH 6.5.

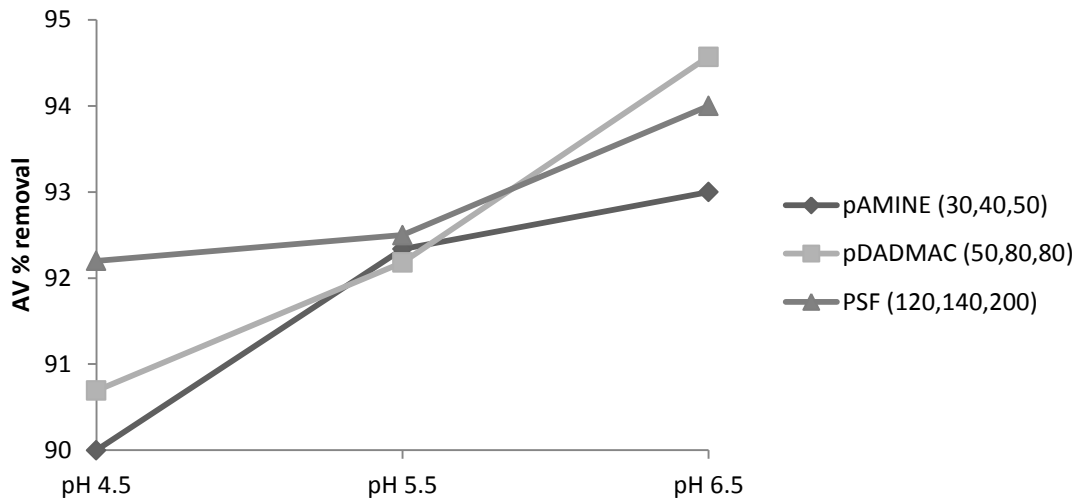


Figure 22. Removal efficiency of turbidity at various optimum dosages pH 4.5, 5.5, and 6.5.

5.3.1 Influence of pH - Discussion

Our results show that the pH of the water had a significant influence on the coagulants performance. Overall at acidic pH values the dosage to be added to achieve optimum purification efficiency were significantly lower than at neutral conditions. Our findings are in line with Yu et al, (2006) who while working with metal salt coagulant and a mixture of metal salt and organic polymers, showed at higher pH (≥ 9.5), the performance of the coagulants was diminished. During our experiment we did not test pH values above neutral; nevertheless we have found out that lower dosages were required as the pH was decreased from 6.5 down to 4.5. There was 20 % drop in dosage requirement with pAMINE, 0 % with pDADMAC and 30 % drop with PFS when pH was reduced from 6.5 to 5.5. When pH was further reduced 6.5 to 4.5 there a 40 %, 37 %, 40 % drop in dosage requirement pAMINE, pDADMAC and PFS respectively. Lower pH favored the removal of T.N with the use of pAMINE, the leaching of T.N in the treated samples reduced from 43 % to 20 % as the pH of the sample water was dropped from 6.5 to 5.5 and down to 10 % at pH 4.

6 Conclusion

From this study it is very evident that cationic polyelectrolytes could be a suitable replacement for the commonly used metal salt coagulant in chemical treatment of wastewaters. Overall they presented satisfactory removal efficiencies and were less affected by temperature, mixing and pH variations. The dosage requirements of the tested organic polymers were significantly lower compared to the inorganic coagulant.

Organic polymers perform relatively well when fast mixing stage was excluded from the treatment process unlike PFS which had its performance greatly affect. Organic polymers have nevertheless showed higher sensitivity to the variations applied during the slow mixing stage of the process although the removal efficiencies were not significantly affected.

Lower temperatures greatly reduced the removal ability of SS, nevertheless the lower percentage removal of T.P, PO₄, turbidity and color stayed above 80 % for all coagulants. Low temperatures though favored the removal of T.N and to a lesser extend TOC.

Lower dosages were required to achieve optimum efficiencies for water samples with lower initial pH. Based on our results it is therefore possible to conclude that lower water pH leads to lower dosage requirements for the coagulants and pH range tested.

Further investigation is recommended for pAMINE and its leaching of nitrogen into the system. Further dosage reduction could be achieved with the use of polyelectrolytes as flocculant aids, hence further research in the combined use of polyelectrolytes as coagulant and flocculant agents is highly recommended.

One of the main concerns of the use of organic polymers is their high cost some authors nevertheless believe that this can be offset by their reduced dosages, less dependence on pH, reduced sludge bulk, and their less susceptibility to mixing.

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Appendix 1

The last row on table A, B, C and D shows the average removal percentages at respective optimum dosages and calculations of the standard deviation.

Table A, - Average % removal at optimum dosage at normal temperature and pH 6.5 (pAMINE, pDADMAC, PFS)

Parameters	pAIMNE	pDADMAC	PFS	Standard Deviation
T. N	-45,7	36	39,1	27,7
T. P	88,7	90	96,1	2,3
PO ₄	90,0	94	97,9	2,3
SS	85,6	87	97,0	3,6
TOC	23,0	38	76,8	16,0
Turb.	93,3	95	95,1	0,6
Colour	83,3	90	95,0	3,4
Fe μ g/l	93,6	94	80,3	4,5
Al μ g/l	89,0	88	88,5	0,4

Table B, - Average % removal at optimum dosages at low temperatures. (pAMINE, pDADMAC, PFS)

Parameters	pAMINE	pDADMAC	PFS	Standard Deviation
T. N	12,50	43,75	59,38	13,8
T. P	85,62	80,82	90,41	2,8
PO4	89,13	91,30	88,04	1,0
SS	70,31	67,50	74,06	1,9
TOC	25,81	38,71	79,68	16,2
Turb.	81,62	81,50	86,72	1,7
Colour	76,88	78,75	84,38	2,3
Fe μ g/l	91,08	91,77	65,38	8,7
Al μ g/l	86,08	86,71	88,48	0,7

Table C, - Average % removal at optimum dosages at pH 4.5. (pAMINE, pDADMAC, PFS)

Parameters	pAMINE	pDADMAC	PFS	Standard Deviation
T. N	-10	10	25	10,1
T. P	69	82	91	6,4
PO4	69	86	90	6,2
SS	82	85	91	2,8
TOC	33	40	63	9,1
Turb.	90	91	92	0,7
Colour	85	88	90	1,4
Fe μ g/l	91	91	47	14,5
Al μ g/l	84	85	91	2,2

Table D, - Average % removal at optimum dosages at pH 5.5. (pAMINE, pDADMAC, PFS)

Parameters	pAMINE	pDADMAC	PFS	Standard Diviation
T. N	-20	10	30	14,5
T. P	86	87	92	1,8
PO4	86	88	90	1,1
SS	86	89	90	1,3
TOC	27	43	72	13,3
Turb.	92	92	96	1,3
Colour	88	88	93	1,7
Fe μ g/l	95	96	27	22,7
Al μ g/l	91	91	91	0,1