Adsorption of Colour from Pulp and Paper Mill Wastewaters onto Diatomaceous Earths

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Abstract

Production of pulp and paper from raw wood involves the washing of substantial quantities of highly coloured material from the wood pulp. Although most of this colour is trapped within the mill and the mills wastewater treatment system, discharge of coloured wastewater remains a problem of public concern.

Lake Rotorua, New Zealand is filled with sediment consisting almost exclusively of diatoms. The most abundant species, *Aulacoseira,* has been shown to have very small pores (< 200 nm) that could be very useful for the capture and holding of large organic molecules. Lake Rotorua is situated close to the two largest pulp and paper mills in New Zealand and may have to be dredged to solve a problem of eutrophication. Wastewaters generated at the Kinleith (Tokoroa) and Tasman (Kawerau) mills in the North island of New Zealand have been used to assess the characteristics of colour removal by Lake Rotorua diatoms.

Vacuum filtration through the diatoms succeeded in removing colour but proved to be impractically slow as an industrial process. Addition of diatoms to wastewater streams in stirred experiments showed that significant adsorption took place. The majority of the colour was removed within 30 seconds of mixing. The efficiency of colour removal was found to vary between wastewater streams within the mills. The pH dependency of this removal was tested and found to be most effective in a pH range of 3.6 to 5.

Attempts to reuse the diatoms showed that chemical backwash regimes were more effective than calcination.

This study concluded that surface silanols were likely to be the principle agent in forming coagulants with the colour material and were subsequently trapped on the diatom surfaces, but more importantly within the pores.

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Abbreviations

General

BSi	Biogenic silica
CPU	Chloroplatinate Unit(s)
DAF	Dissolved Air Flocculation
DE	Diatomaceous Earth(s)
et al.	et alii (and other persons)
GAC	Granulated Activated Carbon
GF/C	Glass Fibre Filter Disc, Grade C
NCASI	National Council of the Paper Industry for Air and Stream Improvement
ppb	Parts per billion
RMA	Resource Management Act (1991)
rpm	Revolutions per minute
SDV	Silicon deposition vesicle
STV	Silicon transport vesicle
UV	Ultra Violet Radiation
Vas	Antisymmetric vibrations
VOH	OH vibrations
Vs	Symmetric vibrations

Techniques and Instruments

EDS	Energy Dispersive X-ray Fluorescence (analyser on scanning electron microscope)
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
IR	Infrared Radiation Spectrometry
SEM	Scanning Electron Microscope
UV/Vis	Ultra Violet Radiation/Visible Spectroscopy
k x	One thousand times magnification

International System of Units (SI) is used for all units of measurement (Aylward and Findlay 2002).

Unless otherwise stated all elements and compounds are expressed in shorthand capital letters e.g. Al for aluminium, Fe for iron and HCL for hydrochloric acid.

Chapter 1

1.1 Introduction

Diatomaceous earths have been used as filters of tannins in foodstuffs and as absorbents in a variety of processes. For this study locally sourced diatoms from Lake Rotorua were mixed with wastewaters from Kinleith (Tokoroa) and Tasman (Kawerau) paper mills. Diatomaceous sediments from Lake Rotorua have been shown to largely consist of the diatom type *Aulacoseira*. *Aulacoseira* diatoms have pore sizes smaller than 200 nm. This material has been investigated as a potential filter and adsorber of the refractory organic material responsible for much or the colour associated with pulp mill wastewaters.

This study sets out to investigate whether these diatoms could be used to remove colour from pulp and paper mill wastes.

Research covering areas applicable to this study are reviewed below. Pulp and paper mill wastewaters are complex in their chemistry and not the subject of this study. This study focuses instead on a novel method of colour reduction in pulp mill wastewaters.

The areas of importance for this study were the volumes of wastewater, types of applicable filtering systems, a review of diatomaceous sediments and diatoms, specifically the Si-OH and Al based diatom structure and active surface groups. The activity of the surface silanols relative to diatom age and structural features are also covered.

1.2 Pulp and Paper Mill wastewaters

The brown colour in bleached kraft mill effluent wastewaters originates from wood handling, chemical pulping and bleaching operations, and is due to tannin, cellulose and lignin derivatives. A typical modern bleach kraft pulp and paper mill produces approximately 20 m^3 of wastewater per tonne of product (Smook 1997; Clark 1999; Wingate 2002).

Wastewaters from two New Zealand Pulp and Paper Mills; the Kinleith mill at Tokoroa and the Tasman Mill at Kawerau were sampled in this study (Appendix 1.a). Both mills have consents to discharge effluents into local waterways and have a proactive attitude to environmental issues with ongoing effluent clean up policies (Kinleith 2002). Wastewater from the mills is often highly coloured (Smook 1997; Wingate 2002; Ali Kanber, Langdon et al. 2004(a); Ali Kanber, Langdon et al. 2004(b)) with discharge volumes around 110 million litres per day (Kinleith 2002). The colour decreases the aesthetic appeal of the receiving water and also reduces the penetration of sunlight through the water column, which may affect photosynthetic rates and therefore aquatic productivity (Smook 1997; Wingate 2002). As a result, there is pressure from environmental regulators for mills to reduce the colour from their wastewater outflows. Because of the large volumes of wastewater involved and the economic constraints this entails there is currently no sustainable colour removal technology available (Wingate 2002).

Cellulose is a long linear polysaccharide composed of anhydoglucose units. Lignin is an amorphous three-dimensional polymeric network of phenylpropane units. The varied or random polymerization that takes place during the biosynthesis of lignin has prevented its exact structure from being elucidated (Wingate 2002). This complexity is further increased by disintegration, polymerization and the re-arrangement that occurs during the pulping process (Clark 1999) and the presence of many phenol types (Diez, Mora et al. 1998). The dark brown/yellow colour of lignin is the result of considerable double bond resonance. As the pH increases, changes in the ionic state of the chromophores alter their absorptivity, thereby increasing the colour of the sample. This is not a linear relationship, but varies on the source and pH of the colour (Wingate 2002). Colour in pulp and paper mill effluents, has been said to be an effect of pH (Wingate 2002; Stuthridge 2006).

The most common colour measurement method in use is that adopted by the National Council of the Paper Industry for Air and Stream Improvement ((NCASI)), USA.NCASI developed the method specifically for pulp and paper industry wastewater. The colour of the filtered sample is determined by taking spectrophotometric readings at 465 nm. The absorbance reading at 465 nm is compared against the standard, a chloroplatinate solution the result expressed as a chloroplatinate unit (CPU) ((NCASI) 1971) (Appendix B, CPU standard).

Colour in wastewater is seen primarily as an aesthetic concern. Colored material also absorbs sunlight, which could reduce the photic depth of the receiving waters and consequently result in an affect on other aquatic productivity due to decreased photosynthetic rates. Another possible environmental concern is the accumulation of the precipitated colour bodies in lower velocity regions of the receiving water with effects on the aquatic communities present (Slabber 1990; Diez, Mora et al. 1998; Wingate 2002).

Physical and chemical processes for colour removal have been extensively studied (Prouty, 1990 summarized in Diez, 1998 and Wingate, 2002) and include coagulation, floatation, sedimentation, biosorption, UV photodecomposition, advanced oxidation, enzyme activity and ultra filtration.

1.3 Filtration

In the simplest of terms, filtration is an operation that is designed to separate suspended particles from a fluid media by passing the solution through a porous membrane or medium. As the solution moves through the voids or pores of the filter medium the solid particles are retained on the surface of the medium or on the walls of the pores, while the fluid (filtrate) passes through.

In surface-type filter media, the solid particles of suspension, on separation are mostly retained on the medium’s surface. That is particles do not penetrate the pores. Filter paper would be a common example of this type of media (Cheremisinoff 1998).

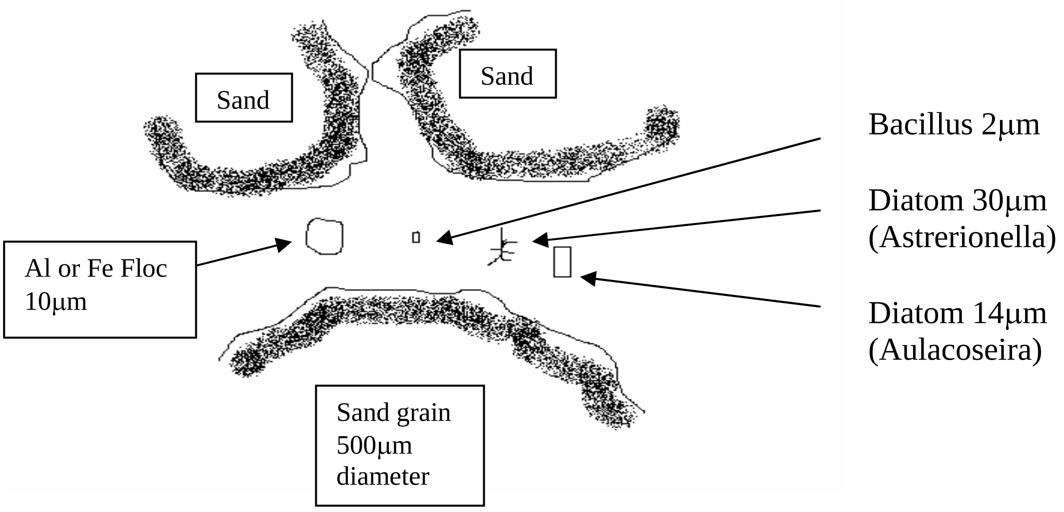


Figure 1.1: *Relative sizes of some filter materials. Adapted from Rushton, 1996.*

Depth-type filters are largely used for liquid clarification. In depth-type filters the solid particles penetrate into the pores where they are retained (Rushton, Ward et al. 1996; Cheremisinoff 1998).

Filter aids and/or flocculants are used to improve the filtration characteristics of hard to filter suspensions, figure 1.1. Filter aids may be applied in one of two ways.

1) The first method involves the use of a *pre-coat*, in which the filter aid is applied as a thin layer over the filter before the suspension is passed through.
2) The second application method involves mixing a certain amount of the filter aid with the suspension (flocculent) before introducing it to the main filter.

In some cases the filter aid displays adsorption action, particle separation of sizes down to 0.1 μm occurs for aids such as bleached earth, diatomaceous earth and activated charcoals (carbon) (Cheremisinoff 1998).

1.4 Coagulation

Coagulation technology involves the addition of a coagulant additive such as alum, ferric salts, calcium or a polyamine to the wastewater stream. Additional chemicals that may be added to enhance coagulation include activated silica, often in the form of a silicate complex made from sodium silicate (Cheremisinoff 1998). Chemical additives alter the physical structure of the suspended solids to the extent that they loose their colloidal nature. Using coagulating salts, insoluble hydrolysis products form which increase the particle concentration and improve the coagulation rate (Rushton, Ward et al. 1996), this is often accompanied by agglomeration forming flocs (Cheremisinoff 1998).

Flocs are formed between the coagulant and the colour targets in the waste stream; it is thought that flocs form a molecular bridge or bridges between target particles to make a polymer type chain (Rushton, Ward et al. 1996). By combination with sedimentation or dissolved air flotation (DAF) the flocs are separated from the liquid (Stumm 1992). Flocculation is generally taken to be a purely physical process in which the treated water is gently stirred to increase inter-particle collisions; this can promote the formation of larger particles. Chemical additives used in coagulation alter the structure of suspended solids to the extent of loosing their colloidal nature and becoming more or less crystalline (Cheremisinoff 1998; Cheryan 1998). Coagulant costs and the resultant sludge disposal are significant deterrent to the application of these technologies within the pulp paper industry (Wingate 2002). In an assessment of coagulants used in pulp and paper mill wastewaters the following conditions were required to remove 90% colour.

Coagulant	**pH**	**Dose (mg L^{-1})**
Alum	4.4 – 6	180
Aluminium chloride ($AlCl_3$)	6	180
Ferric chloride ($FeCl_3$)	4.4 – 6.1	400
Lime	> 11	3 000

(Wingate 2002)

The results of Al and Fe salts (Stumm 1992) used as examples for the effects of coagulant and colloid concentrations are explained in the terms of zones:

1) Sufficient coagulant over saturation, to produce a rapid precipitation of a large quantity of the Al or Fe hydroxide. These hydroxides enmesh the colloidal particles in what is termed a “sweep floc”.

2) At the other extreme are very high colloid concentrations of the order often encountered in sludge or wastewater treatment plants. High coagulant dosage is required to destabilize the colloid. The dosage may equal or exceed that required for precipitative coagulation of dilute suspensions.

3) For systems with low colloid or low coagulant concentrations it is proposed that insufficient contact opportunities exist to produce aggregates or flocs within a reasonable detention time, as in low turbidity waters.

4) The final zone is that where increasing colloid concentrations requires an increasing coagulant dosage; that is, a stoichiometry in coagulation is observed (Jones 1989; Stumm 1992). It is suggested that in low turbidity waters the addition of bentonite (a finely divided clay) and some forms of activated silica have proved effective (Stumm 1992).

1.5 Pulp wastewater colour removal technologies

Activated carbon has been shown to be an effective adsorptive colour remover. The carbon is activated usually by heat or chemical treatment; the adsorption is often so strong that the carbon has to regenerated or even discarded. Activated carbon in industrial treatments is more applicable with other technologies for example with DAF. DAF is used to remove the carbon from solution (Wingate 2002). Granulated activated carbon (GAC) has also been suggested as a complimentary technology with diatomaceous earth packing based filters. GAC is used first, as a coagulant, to remove the colour and diatomaceous earths to remove the GAC (Glanville 2005). Adsorption media cost and sludge production are factors limiting the application of this technology to the pulp paper industry (Diez, Mora et al. 1998; Wingate 2002).

Allophane is a non-crystalline hydrous aluminosilicate characterized by a short range ordered nature and Si-O-Al bonds. Using allophane the suggested method of binding to organic matter is via the active FeOH and AlOH sites. Allophane has been determined to have a high surface area (310-672 m^2 g^{-1}) allowing an adsorption capacity comparable to activated carbon. Figures of >86% colour removal within the first five minutes when mixed with pulp mill wastewaters are given. The allophane was stirred or shaken in a flask with the mill effluent (Diez, Mora et al. 1998).

1.6 Diatomaceous Sediments

> ‘Diatomaceous sediments (or earth) is light coloured, porous and composed of the siliceous frustules of diatoms found in earthy beds that somewhat resemble chalk.
>
> It is lighter than chalk and will not effervesce in acid. When well hardened it is called diatomite. Diatomite contains approximately 8 million diatom frustules per cubic cm. The deposit of Lompoc, California, U.S. covers 13 square kilometres and is up to 425 metres deep.

> Diatomite is relatively inert. It has a high absorptive capacity, large surface area, low bulk density, and relatively low abrasion. It consists of approximately 90 percent silica, and the remainder consists of compounds such as aluminium and iron oxides. The fine pores in the frustules make it an excellent filtering material for beverages, chemicals (sodium hydroxide, sulphuric acid, gold salts), industrial oils (those used as lubricants or in rolling mills or for cutting), cooking oils (vegetable and animal), sugars (cane, beet, corn), water supplies (municipal, swimming pool, waste, boiler), varnishes, lacquers, jet fuels, and antibiotics, to name a few. The low abrasive properties make it suitable for use in toothpaste, "nonabrasive" cleansers, polishes (silver, automobile), and buffing compounds.
>
> Diatomite is widely used as a filler and extender in paint, paper, rubber and plastic products; the gloss and sheen of "flat" paints can be controlled using diatomite. During the manufacture of plastic bags, diatomite added to the newly formed sheets to act as an antiblocking agent so that the plastic (polyethylene) can be rolled while it is still hot. Because diatomite can absorb approximately 2.5 times its weight in water, it also makes an excellent anticaking carrier for powders used to dust roses or for cleansers used to clean rugs. Diatomite is also used in making welding rods, battery boxes, concrete, explosives, and animal food.'
>
> (Britannica 1999)

Diatomaceous earths (DE) have been used as filters for many years, the U.S. Geological Survey Press reporting a total of 4,593 tons of diatomaceous earth was produced and sold in the United States in 1915. The U.S.G.S. reports a considerable amount of this diatomaceous earth being used by sugar refiners for filtering, fining and clarifying (Anon 1916).

Filtration systems are varied in design, operation, and application. As a finer (clarifier) diatomaceous earth is spread as a powder over the liquid to be fined. Clarification will occur simply by the movement of the particles through the liquid. (Julier 1993; Singe and Cheryan 1998).

Filters operate not only because of pore size but also by a certain amount of adsorption. Diatomaceous earth as a filter aid increases the functional life of a filter by retarding pore clogging. DE acts as packing on the filter (a metal screen or fabric) increasing the filters ability to trap suspended solids. When full the DE can be easily removed from the filter structure and new DE added or a backwashing procedure used. Filtration is achieved by the many fine pores in the frustules or by spaces between the packed diatoms (Broom, Squires et al. 1992; Rushton, Ward et al. 1996; Sui and Huang 2003; Westfall 2005)

There are numerous literature references to the use of diatomaceous earth in filter applications utilizing the pore size for entrapment or the surface adsorption onto active surface sites. Where adsorption is required young diatoms, generally from cultured sources are used, as the active silica sites have not degenerated. Examples are the nucleic acid-binding property of diatomaceous earth (Hubbard, Cann et al. 1995), capture of plasmid DNA, due to adsorption on to diatomaceous earths (Theodossiou, Collins et al. 1997) and the ability of diatomaceous earth to retain metals such as Cd, Cr, Mn, Pb and Hg (Schmitt, Muller et al. 1999; Cabanero, Madrid et al. 2002).

1.7 Diatoms

Diatom is the name given to the species of photosynthetic algae of the class Bacillariophyceae. Though present in terrestrial environments, their main habitat is aquatic. Diatoms can be found in freshwater and marine water, generally occupying the top 100 metres, where sunlight is available. There are 10^4 species of diatoms known in taxonomy, based on the variety of the exoskeleton or frustules morphology. These frustules are composed of two halves that fit together, the epivalve and hypovalve; the connective section is termed the girdle bands (Images 1.2 to 1.6). (Vinyard 1979; Round, Crawford et al. 1990).

The frustules are composed of amorphous, porous, hydrated SiO_2 or biogenic silica (BSi) (Smol, Battarbee et al. 1986; Round, Crawford et al. 1990; Gehlen, Beck et al. 2001).

Valve formation begins within the mother cell where each of the two new daughter cells develop a new hypovalve and girdle bands in a special cellular compartment, the silicon deposition vesicle (SDV). During the growth and maturation of the new valves, silicon transport vesicles (STV) are used to transport silica precursors to the SDV from the cytoplasm. The STV's fuse continuously with the expanding SDV, until the valves, hymen and girdle bands, are excreted. Before excretion the siliceous parts are coated with a protective layer of proteins and carbohydrates that stop spontaneous dissolution of the valves in the aqueous environment (Round, Crawford et al. 1990; Vrieling, Beelen et al. 1998).

Vrieling suggested that the silica precursors are transported to the SDV via acidic STV's. Acidification of the SDV allows a thermo-dynamically driven fast aggregation of silica particles to form the final valve and girdle bands, less than 8 hours for the completion of a new hypovalve. The advantage of the low pH in the SDV for diatoms is that the formed siliceous parts are protected from continuous dissolution that may destroy fragile or important details such as ribs and spiculae (Vrieling, Beelen et al. 1998).

When diatoms die their silica-rich cell walls (exoskeletons) generally remain intact and accumulate in the sediments as diatomaceous 'ooze' (Rankama and Sahama 1950; Round, Crawford et al. 1990; Gehlen, Beck et al. 2001). These sediments are often referred to as diatomaceous earths, kieselguhr, diatomite or biogenic silica (BSi) (Vrieling, Beelen et al. 1998) (Garrels and Mackenzie 1971; Kaufman 1993; Gehlen, Beck et al. 2001).

Many processes have been applied to aged diatomaceous earths and fresh cultured diatoms to ascertain the morphology, silica structure and mechanisms used by the organism. The age of most diatomaceous earths used in these comparisons is thousands to millions of years old. Reactions occurring during that time result in destruction of attractive morphological features and surface silanol sites (Ellwood and Hunter 1999; Dixit and Van Cappellen 2002), while contaminating minerals and detritus are also incorporated into the sediments (Schluter and Rickert 1998).

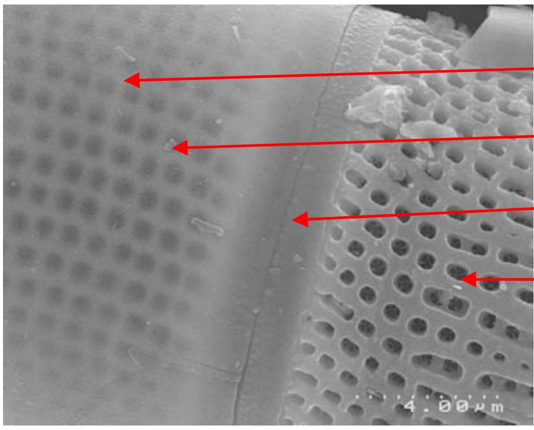


Image 1.2
Epivalve (epitheca)

Hymen layer, over epivalve

Girdle band (cinture)

Hypovalve (hypotheca)

(Diatom type-Aulacoseira)

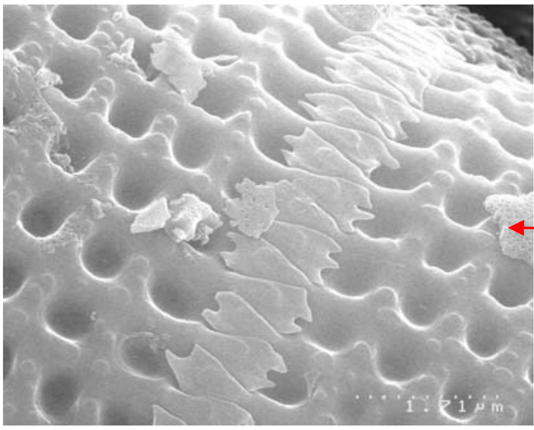


Image 1.3

Two daughter cells joined at the hypovalves
Scale: 1.71 μm (15k x magnification)

Small piece of diatom hymen

(Aulacoseira)

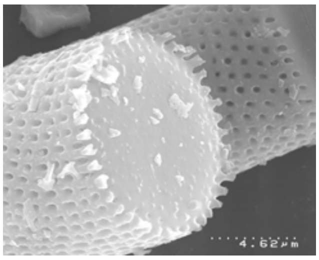


Image 1.4:
Separation valve
Scale: 4.62 μm
15k x magnification

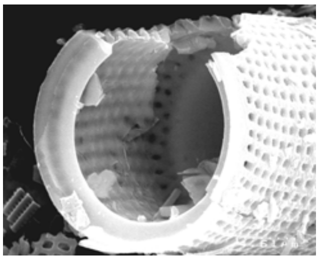


Image 1.5:
Girdle band
scale: 4.61 μm
15k x magnification

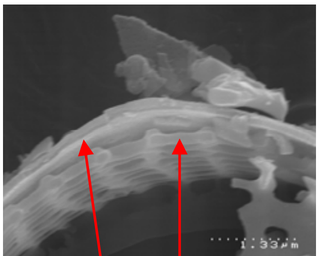


Image 1.6:
Hymen Thecae
scale: 1.33 μm
60k x magnification

(Aulacoseira)

Diatom chemical composition

Experiments into the surface site density, deprotonation constant and Al (aluminium) surface complex formation constants have been undertaken on fresh cultured diatom surfaces and aged biosiliceous material with synthetic amorphous silica as a control. At the pH range encountered in the oceans and marine pore waters, the surface charge density of aged biogenic silica was significantly lower than that of the cultured diatoms. It is suggested that the dissolution of the unprotected exoskeleton remains, results in a decrease in the abundance of ionizable surface silanols (Dixit and Van Cappellen 2002). It has been well established that dissolution kinetics of minerals are related to surface charge (Stumm 1992). This may explain the observed decrease in reactivity, or aging, of biogenic silica during settling through the water column and subsequent burial in sediments (Dixit and Van Cappellen 2002).

Al-Degs *et al* (2000) using Jordanian sourced diatomite (Aulacoseira) give as part of the chemical composition SiO_2 72%, Al_2O_3 11,42%, Fe_2O_3 5.81 % Na_2O 7.21 % and CaO 1.48 %. Celite® a propriety diatomite filter aid has a typical natural state chemical analyses of, SiO_2 85.5%, Al_2O_3 3.8%, Fe_2O_3 1.2 % Na_2O + K_2O 1.1 % and CaO 0.5 % (Rushton, Ward et al. 1996). Al within the Si (silicon) matrix can reduce the solubility of the biogenic silica.(Gehlen, Beck et al. 2001).

X-ray absorption spectroscopy investigations on diatom frustules indicate a structural association between Al and Si. In samples of cultured diatoms, Al was present exclusively in fourfold coordination at less than 1% Al (Gehlen, Beck et al. 2001). Vrieling *et al.* (1998) found similar concentrations of Al within the SiO_2-matrix. Schluter quotes an Al content of 6%, for siliceous frustules sampled in sediments of the Zaire deep-sea fan, reported by Van Bennekom *et al.* (1989). Utilising different extraction techniques, with respect to the pH of the leaching agent, the assumption was that BSi is almost completely dissolved after 2 h of extraction. From the aluminum released an estimate for the Al content of the biogenic silica of 0.1 to 0.8% was suggested for the marine sediment investigated (Schluter and Rickert 1998).

Using X-ray adsorption, the location and relative intensities of features, suggest that the organism synthesizes the structural insertion of tetrahedral Al inside the silica framework; four coordination in cultured diatom specimens. The peculiar structural position off Al within the BSi framework is invoked to explain the inhibiting effect of Al on the solubility of BSi (decrease of solubility). The same experiments found that in natural diatom samples, Al is present in mixed six- and four-coordination. The relative intensities of XANES structures indicate the coexistence of structural Al with a smectite or illite component. The six coordination of Al was reported as consistent with adhering mineral particles that may be occluded in frustule pores (Gehlen, Beck et al. 2001). Six-coordination is considered uncommon and in most cases is the result of extreme pressure and temperature. The mineral known as *stishovite* formed in meteorite impacts being an example (Mackay, Mackay et al. 2002).

The natural biomineralization of silica conforms to the accepted rules known in 'classical' silica chemistry. Although some contamination with Al and Fe is reported the indications are that diatoms produce a nearly pure SiO_2 matrix(Vrieling, Beelen et al. 1998). A wide range of Si(OH) silicates is known and in almost all cases the coordination number of silicon with respect to oxygen is four. The vast majority of silicates are built up from SiO_4 tetrahedra (Fig 1.2), by sharing zero, one, two, three or four vertices with other SiO_4 (or MO_4) tetrahedral.

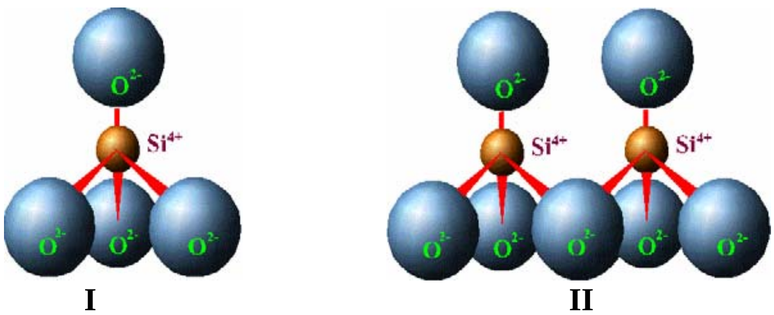
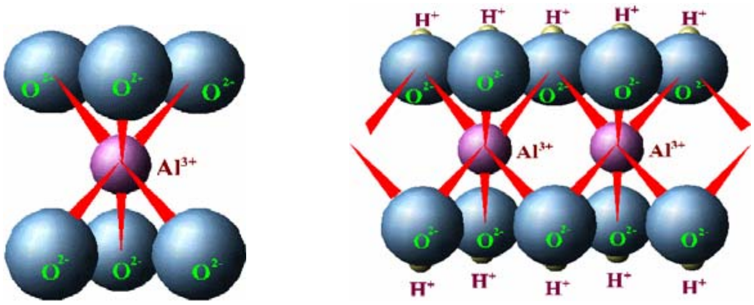


Figure 1.2: I, *SiO_4^{4-} tetrahedron sheet:* **II,** *silicon tetrahedron* (Burridge 2006)

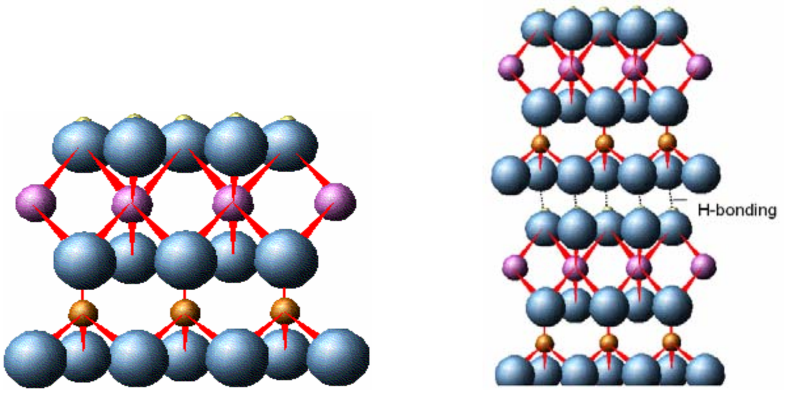
When SiO_4 shares three vertices sheet structures are formed ($Si_4O^{4-}_{10}$), an example being *talc* $Mg_3(OH)_2Si_4O_{10}$. The sheets are held together by weak van der Waals forces and can be considered similar to graphite. A common occurrence in silicates is for one element to substitute for another of the same size. An important substitute is that of aluminium for silicon. Aluminium is a 3^+ ion, silicon is a 4^+ ion, and hence an additional cation is required for charge balance (Fig 1.3). Potassium (K+) is 1^+ ion thus in the silicate framework an Si^{4+} can be substituted by an Al^{3+} and a (non framework) K^+. An example would be the *mica's* such as *phlogopite* $KMg_3(OH)_2Si_3AlO_{10}$.



I II

Figure 1.3: I, *Octahedral aluminium unit:* **II,** *Gibbsite* (Burridge 2006)

When all four SiO_4 oxygen atoms are shared with adjacent tetrahedral this gives the 3-dimentional structure of SiO_2. As all the oxygen atoms are shared (no terminal SiO-) there will be no charge (e.g. quarts or cristobalite). Si can be replaced by Al as in the sheet structures to give aluminiosilicates for example *feldspar* minerals ie *orthoclase* KAlSi3O8. Four coordination of SiO4 (Fig 1.4) is also the foundation structure of *Kaolinite* and *zeolites* (Voronkov, Mileshkevich et al. 1978; Mackay, Mackay et al. 2002).



I II

Figure 1.4: I, *Micelle, aluminium and silica in sheet:* **II,** *Kaolinite* (Burridge 2006)

Diatoms have many similarities to *zeolites* (Vrieling, Beelen et al. 1998) with the suggestion from compositional analysis of diatom samples that calcium (Ca^{2+}) and a great many other cations are used as a charge compensator as opposed to K^+ (Garrels and Mackenzie 1971; Gehlen, Beck et al. 2001). Iler (1971) suggested that calcium in silica structures was dependant on the concentration of metal salts and pH, although Iler quotes Kolthoff & Stenger who reported that the calcium ion was adsorbed as the aquo-ion and involves the formation of coordinate linkages suggesting the replacement of NH3 molecules by OH groups as one possible mechanism and therefore may be the result of other surface chemistry reactions, not charge balance (Iler 1971).

If the substitution occurs in the tetrahedral sheet, the resulting negative charge can distribute itself over the three oxygen atoms in the tetrahedral in which Al (III) has substituted the Si. The charge is localized and relatively strong inner-sphere surface complexes can be formed, i.e. with K^+. If the isomorphic substitution occurs in the octahedral sheet, substitution of Al (III) by Fe or Mg (Voronkov, Mileshkevich et al.). The resulting negative charge distributes itself over the ten surface oxygen atoms of the four silicon tetrahedral that are associated through their apexes with a single octahedron. The distribution of the negative charge this way enhances the Lewis base character of the ditrigonal cavity and makes it possible to form complexes with dipolar molecules as well as with cations such as Ca^{2+} (Stumm 1992).

Diatom sedimentation

As sedimentation proceeds, burial of diatom skeletal remains results in a competition between preservation of the BSi or dissolution to the silica under-saturated waters. The ongoing dissolution is revealed by the build up of silicic acid ($Si[OH]_4$) in pore waters to semi-constant levels from below 5 to 30 cm (Gehlen, Beck et al. 2001).

There is a lowered apparent solubility in the sediments of the BSi that does not reflect the thermodynamic equilibrium between pore waters and the dissolving phase. The term 'reverse weathering' is used by Gehlen *et al* (2001) quoting work by Mackenzie & Garrels (1966) referring to the uptake of $Si(OH)_4$ from dissolving BSi through the formation of aluminosilicate minerals (Image 1.7 & 1.8), other examples are also given (Garrels and Christ 1965; Pollard and Weaver 1973). Michalopoulos & Aller (1995) and Dixit et al. (2001) verified experimentally reverse weathering and aluminosilicate formation (Gehlen, Beck et al. 2001).

This process alone, however, cannot account for the apparent low solubility of BSi in marine sediments. After removal of the organic matrix, Al is the most important factor regulating the solubility of BSi (Gehlen, Beck et al. 2001) , aluminium and other cations should be accounted for when considering the results from experimentation with diatoms.

The age of the diatom frustules is of importance, with fresh cultured diatoms having more active silanol sites. The effects of digenesis, general aging and reverse weathering may need to be allowed for, the results of which may be inclusion of aluminium, iron and other potential reactive compounds.

1.8 Lake Rotorua - Diatomaceous sediment source

Water quality is a global issue; in recent years widespread changes in water quality have been recorded, the deterioration monitored is often a result of the effects of land use change and population increase.

In New Zealand the deterioration of the quality of water in lakes of the Rotorua District is a serious problem. All of the twelve major lakes in the region show decreasing water quality from the results of nutrient overload, levels of nitrogen and phosphorus have been increasing over the past few decades, with the trend expected to continue.

Lake Rotorua is the largest in the group, with the region's main population center, the City of Rotorua situated on the shores of the lake's southern end. The lake is currently a productive trout fishery and is one of the main tourist attractions for the wider region. Lake Rotorua is situated in a near circular volcanic caldera, surrounded by ignimbrite rocks of the Mamaku Plateau and has been affected in recent geological time by a series of pumice ash showers. Lake Rotorua is fairly shallow with a mean depth of 10.5m and a maximum depth of 26 m (Note: small 44m crater). The lake area is 80 km^2 with a volume of 802 Hm^3 (Beya, Hamilton et al. 2005), appendix A-1 and 2, maps.

In Lake Rotorua excess nitrogen and phosphorus has stimulated the growth of phytoplankton and has eventually led to poor water clarity and blue-green algal blooms (Cassie Cooper 1996; Hamilton, Alexander et al. 2004; Beya, Hamilton et al. 2005). Health warnings are now issued routinely during summer for parts of Lake Rotorua in response to blue-green algal cell counts exceeding recommended recreational limits (Beya, Hamilton et al. 2005). Phosphorus is concentrated in the sediments, typically 1500 g/tonne but up to 3000 g/tonne in the top 2 cm. Algal blooms are considered a response to the recycling of this phosphorus from the sediments to the water column (Hendy 2005; Miller 2006).

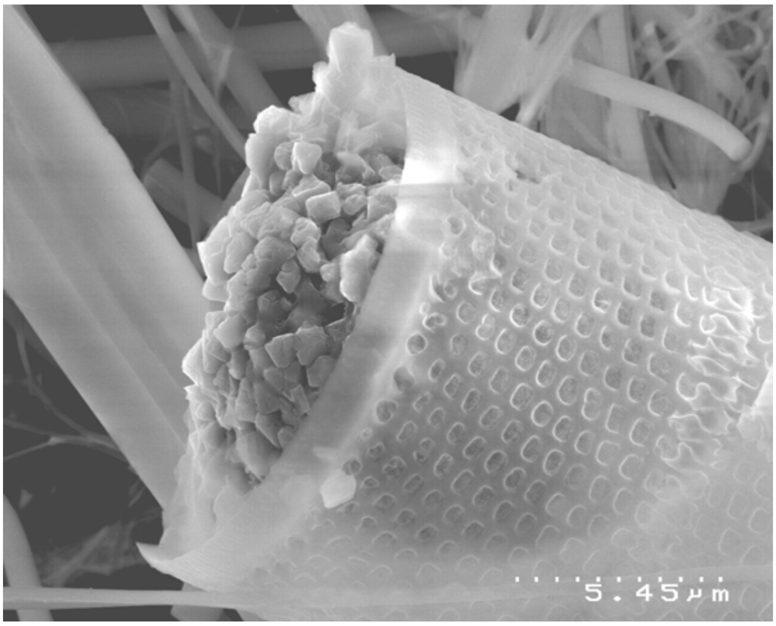


Image 1.7
Framboid formation within Aulacoseira
An example of reverse weathering, courtesy of C. Mangen (Mangen 2006)

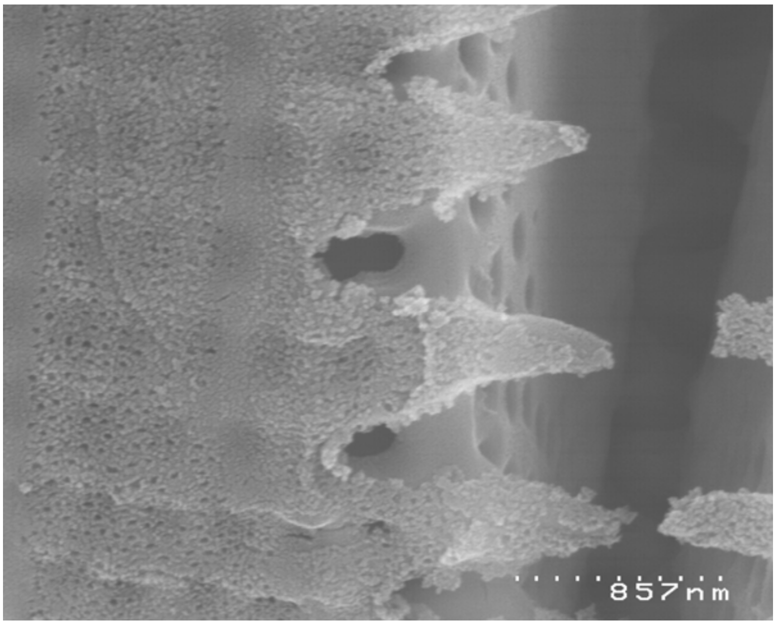


Image 1.8
Weathering of the outer hymen layer on Aulacoseira. Sample taken from a depth of 120mm and below the Tarawera (1886) tephra, courtesy of L. Pearson (Pearson 2006)

A potential management option for Lake Rotorua is dredge removal of phosphorus-laden sediments as a method of reducing the nutrient load on the lake waters. This would lead to the disposal of millions of tonnes of sediment the bulk of which consists of diatomaceous ooze. Present estimates are that 40 % of the lake bottom is covered with diatomaceous ooze, confined to water depths of greater than 10m (Hendy 2006).

Dredging of the sediments in lake Rotorua is an issue still under consideration by the appropriate local (Rotorua District Council) and regional (Environment Bay of Plenty) councils and may or may not prove a viable option (Miller 2006). To be successful knowledge of the composition of the sediment layers is required as removing top layers has the potential to expose lower layers that may have accumulated other undesirable material such as heavy metals from geothermal and volcanic inputs. Stirring of the sediments by the dredge head could lead to increased water turbidity and a release of contaminates which may be harmful to lake aquatic communities (Hartley 2005; Hendy 2005).

For dredging to precede, resource consents need to be granted, the Resource Management Act 1991 (RMA) as the guiding legislation has procedures to ensure any effects are remedied or mitigated. Once the material has been removed from the lake, appropriate storage sites and management strategies should be instigated to ensure a new suite of land-based problems do not occur. In the case of Lake Rotorua there would be millions of tonnes of dredged sediments, initially as slurry piped from the dredge head to land based storage-containment sites. A question that has been asked is whether uses could be found for this slurry? (Miller 2006).

With bulk and unrefined products, transportation is often a major cost (Hoyle 1999). The two paper mills from which wastewater samples in this study were taken are within a 50 km radius of Lake Rotorua, thus the opportunity was presented to investigate the potential of utilizing one waste, Lake Rotorua sediments, to treat another waste, pulp mill wastewaters.

Chapter 2
Materials and Methods

2.1 Materials

2.1.1 Bleached Kraft Pulp Mill sampling

Sampling for this study occurred over a period of 18 months, the effluent wastewaters were collected from bleach Kraft pulp mills in Kawerau and Tokoroa, New Zealand. There are many operation variables that affect the effluents from a bleached Kraft pulp mill such as production demands, spills and other internal operating conditions. These often result in recognizable pH and CPU colour peaks recorded as part of the mills internal monitoring systems. The samples collected were consistent with the average CPU and pH for the month of collection using the mills internal records.

Sample Sites

Kawerau

Tasman mill

- Inflow to oxidation ponds (T-inflow)
- Outflow of oxidation ponds, to Tarawera River (T-outflow)
- Continuous digesters, 3 sample sites.

Tokoroa

Kinleith mill

- Drains 2 & 3 at the start of the open culverts (K-2, K-3). Drain 2 was the acid waste (average 2 – 4 pH) and drain 3 the caustic waste (average 9 – 11 pH).
- 2/3 drains at mixing, east side of road culvert (K-2&3 mix)
- Sand trap 1
- Drains 2/3 inlet pond 19 (K-inflow)
- Outlet pond 19

(Appendix A-1)

The drain K-inflow is of similar constitution to T-inflow being mixed acid and caustic with an average pH of 6 to 8.

The water samples were collected in screw capped 2.5 L glass Winchesters and 20 L plastic containers. The 2.5 L glass Winchester samples had 0.1 % of sodium azide, as a preservative added (Ali Kanber, 2004). Before use all glass and plastic ware had been washed with and soaked in dilute HCL, then rinsed thoroughly with hot water followed by distilled water. All water samples were stored at 4 ^{o}C until required.

2.1.2 Diatomaceous Sediment Samples

Diatomaceous ooze samples were collected from the sediments of Lake Rotorua, New Zealand. The Rotorua area is geothermal and has had a high number of past volcanic events. These events have been dated and are visible as known layers in the local earth horizons. The uppermost tephra layer in the lake sediments consists of Tarawera tephra from the Tarawera eruption of June 1886 (McLauchlan 1992). Sediment samples were taken from 8 sites in lake Rotorua using a 100 x 100 x 1200 mm stainless steel box corer. The sediments above the Tarawera tephra were used, this being typically the top 100mm of the box corer sample. The age of the diatomaceous earths collected can be taken as less than 120 years. This young age and the high deposition rate of the sediments (Hendy 2005) results in the samples averaging > 90 % diatoms as an ooze. The sample sites are detailed in appendix A-3.

After collection the samples were washed with distilled water and then dried at room temperature. Slow drying being recommended over heating to rapidly remove water as high hydrostatic pressure within the pores can lead to detrimental structural changes reducing the reactivity (Iler 1971; Jones 1989).

The dried diatomaceous ooze has a consistency similar to talcum powder, being a very fine dust with a light gray tinge. After drying of the selected box corer samples they were thoroughly mixed. This mix being referred to as the raw or bulk mix, all the diatom samples used in this project were taken from this homogenous mix. The bulk was remixed after any samples were taken.

Because of the high diatom concentration in the sediment samples the term diatoms, unless otherwise stated, is used in this text when referring to samples taken from the dried sediment bulk. This is in fact dried diatomaceous ooze with included sands and tephra.

2.2 Equipment

UV/Vis

A Jenway 6305 UV/Vis spectrophotometer was used to measure absorbance. All samples were filtered through a GF/C filter before measuring the absorbance. The filters were washed with copious amounts of distilled water to remove any loose glass fibers that may upset the absorbance readings. Matched 1 cm quartz cells were used, with all absorbance reading for each sample and UV/Vis frequency taken against distilled water blanks, absorbance readings were taken until two consecutive readings of the same value were achieved. Unless otherwise stated double experiments were run of all stirred mixes, tabled and graphed results record the average of the results obtained. Errors in absorbance are +/- 0.005 nm.

The absorbance frequencies of 350 and 440 nm were selected to allow comparison with the results of Ali Kanbar (2004, a & b), 350 nm as a basic indication of phenolic compounds (Diez, Mora et al. 1998). 400 nm was measured as a bridging frequency from 350 to 440 nm. 365 nm from the CPU standard, and 480 nm for an upper limit above 465.

pH

EDT Instruments, Series 3, BA 350 pH meter was used, operated and calibrated as per the manufacturers handbook. Errors in pH are +/- 0.05. Readings for pH were taken concurrently with absorbance measuring and from the same sample.

ICP-MS

Laser ablation of solid samples and mass spectral analysis of solid and liquid samples was achieved using an ELAN DRC ii ICP Mass Spectrometer.

Laser ablation was performed at full power, 30 J/cm^2 – 0.215 MJ. The laser ablation sites were spaced at 100 μm apart, the laser operated for 5 seconds per site with an average spot ablation site size of 30 μm. Solid samples were compacted using a KBr disc press into wafers, 10 mm diameter by 0.5 mm thick, using 8 tonnes pressure. Twelve laser ablation sites along a straight transect were selected across the disc. Liquid samples were diluted 10:1 with distilled water passed through a Barnstead E-pure water treatment system, then filtered through Millipore 0.45μm filters. ‘A’ grade glass pipettes and flasks were used throughout. Merck standard xxi was used for liquid samples; errors were Al 50 ppb, Fe 500 ppb, Ca 5000 ppb and K 50 ppb.

IR

Infrared results were obtained using a Scimitar Series DigiLab FTIR in full scan mode; data was modeled with Varian Resolutions 4.0 software. Samples were mixed at approximately 6:1 with KBr by grinding with a morta and pestle. The samples were then compacted into wafers, 10 mm diameter by > 0.25 mm thick, using 8 tonnes pressure.

SEM

A Hitachi S-4100 Field Emission Scanning Electron Microscope (SEM) with x-ray analyser (EDS) was used. The samples were attached to stainless steel slides using adhesive carbon tape and coated with platinum. The samples averaged 5mm^2. Examination of the slides at 700x magnification followed overlapping transects and using up to 300Kx magnification if more clarification was needed. Where applicable EDS scans of the samples were made.

2.3 Methods

2.3.1 Packed Column Filter

Glass Column

- The glass column dimensions were 350 mm long by 45 mm inside diameter.
- A glass wool wad (filter-medium) was placed into the column above the outlet valve before the diatoms were added.
- 20 grams of diatoms were packed into each column. When wet the diatoms expanded within the column to a length of 40 - 45 mm.
- The column was placed on a Buckner funnel and vacuum applied to increase the elution time, the vacuum was a laboratory internal line supply of approximately one atmosphere.

Wastewater samples were added to the columns in 100 or 250 ml aliquots. The UV/Vis spectrum of 420 nm was used to measure colour. The pH of the samples was 7.4.

2.3.2 Stirred adsorption, diatoms mixed with mill wastewaters

Liquid filtration is designed to separate suspended particles from a fluid medium by passing the solution through a porous membrane or mixing with a filtering medium (Cheremisinoff 1998). In the column filter the fluid or suspension was forced through the pores or voids of diatomaceous earth. The solid particles were retained on the medium, while the fluid, referred to as the filtrate, passed through. In the stirred experiments the diatoms are mixed within the waste suspension, bringing in new design parameters and variables.

The main parameters and variables considered for these experiments were

- Stirring speed and time
- Sample acquisition times
- Sample analysis (main types; absorbance and pH)
- Diatom effects on absorbance and pH
- Sample wastewater effects on absorbance and pH

Effects such as the contact time of diatoms to waste, adsorption and ion exchange all contribute to the affect on the wastewater. It is likely that the efficiency of adsorption would increase with increased diatom to wastewater ratios. For this to be a useful technique it is necessary to define the efficiencies as a function of ratios were colour removal and rate of removal are considered against diatom to wastewater rates and the cost associated with increasing diatom amounts.(Garrels and Christ 1965; Rushton, Ward et al. 1996; Cheremisinoff 1998).

All the mixing experiments were undertaken at 20 to 22^{o} C in 250 ml flat bottom flasks and stirred magnetically.

The type of filter mechanism envisioned was a stirred flow clarification type with gravity settling at the outflow (Smook 1997; Cheremisinoff 1998). This was considered best suited to the volumes and site positioning for any workable filter. Gravity settling of samples was used as this best represented the affects expected in a gravity-settling outflow.

Sample acquisition from stirred mix experiments

A small aliquot was removed (approximately 5ml) at the selected sample time, allowed to settle (12 hours), and filtered through a GF-C filter, pH and the absorbance measured. Less than 0.5 ml of wet diatoms settled out in the sample aliquots, if dried this would be insignificant in weight. Over the duration of the experiments new wastewater was added to keep the liquid volumes at specified levels, this was approximately 15 ml per 100 ml of wastewater sample. The zero time readings are for the stock wastewater solution before the addition of any diatoms.

Diatom settling rate

There were many diatom frustule parts in the sediment samples less than 45 μm in size (images 3.2, 3.3, 3.4, 3.17, 3.18 and 3.21) that could pass through the GF-C filters used and possibly affect the absorbance readings. As a measure of diatom settling rates and the effects on UV/Vis absorbance, varying amounts of the diatomaceous sediments were magnetically stirred for 2 hours with 100 ml of distilled water in 250 ml flat-bottomed flasks and then allowed to settle. Absorbance readings at 350, 400, 465 and 480 nm were taken of the aqueous phase every hour for 15 hours as the solution settled.

Sample degradation

Wastewater sample aliquots had absorbance readings taken at the start, during and at the end of each experiment mix. The results were used to determine waste degradation independent of all dosing during the experiment and built in to the errors.

100 ml of wastewater from each sample site was stirred for 12 hours and left to stand. Samples for absorbance readings and pH were taken every hour for fifteen hours during the settle period.

Diatom effect on pH

5, 6 and 8 g of diatoms were stirred magnetically with 100 ml of distilled water in a flat bottom flask, the pH being read at 2, 4, 6 and 12 hours.

Change in wastewater colour with change in pH

The colour of pulp and paper wastewater changes with pH. This change may be a significant affect. The pH of wastewater samples was adjusted from 2 to 11 and the absorbance measured.

100ml of Tasman pond inflow (a mix of acid caustic and neutral wastewaters flowing into the first Tasman mill oxidation-settling pond), 100 ml of Kinleith acid and 100ml of Kinleith caustic wastewaters were adjusted for pH with 1% HCL in deionized water and 1% NaOH in deionized water (CPU, Appendix B). Absorbance at 480, 465, 440, 400 and 350 nm were measured.

Change in wastewater pH and absorbance by addition of distilled water

Wastewater was diluted with distilled water to ascertain if pH or absorbance of the wastewater was affected other than by dilution affects. 50 ml of wastewater was magnetically stirred with 100 ml of distilled water for 2 hours then allowed to settle for 12 hours before sampling.

2.3.3 Neutral pH Wastewater

Tasman Mill, settling pond inflow (Tasman inflow)

Experiment 1a: Single dose of diatoms

A series of stirred mixtures was undertaken, 100 ml of inflow waters in 250 ml flat bottom flasks were magnetically stirred for 12 hours with varying amounts of diatoms ranging from 0.25 to 10 grams. The samples were left to stand for 12 hours before CPU tests. As the mechanism of colour removal by the diatoms was not known at this stage a slow stir speed was used, sufficient to keep the diatoms in suspension. Rotational stir speed can affect the rotational shear of the liquid and the filtering by diatoms due to changes in the Zeta potential (Rushton, Ward et al. 1996).

Samples from each stir method were then analyzed using the Chloroplatinate Standard (Appendix B, CPU standard).

Experiment 1b: Single dose of diatoms

Separate mixes of 100 ml of wastewater sample with 5, 6, 8 and 10 g of diatoms. Sample aliquots for absorbance and pH were taken every 2, 4, 6 and 12 hours.

Experiment 2: Double dose of diatoms

Separate mixes of 100 ml of wastewater sample with 5, 6, 8 and 10 g of diatoms. After 12 hours of stirring 5 g of diatoms was added to the initial 5 g and 2 g of diatoms to the 6 g, this took the 5 g to 10 g and the 6 g to 8 g. Sample aliquots for absorbance and pH were taken every 2, 4, 6 and 12 hours from the start and after the addition of extra diatoms.

Experiment 3: Multiple doses of wastewater

8 and 10 g of diatoms initially stirred with 100 ml of wastewater; then at every 12 hours stirring an additional 50 ml of wastewater was added until 250 ml of total wastewater. The solution was stirred for a total time of 48 hours.

Sample aliquots for absorbance and pH were taken every 2, 4, 6 and 12 hours from the start and after each 50 ml wastewater addition point.

2.3.4 High pH wastewaters

Kinleith caustic, Tasman caustic and continuous digesters

Experiment 4: Single dose of diatoms

10 g of diatoms were initially stirred with 100 ml of caustic wastewaters from Kinleith and Tasman mills and 100 ml of continuous digester wastewaters from Tasman mill. Sample aliquots for absorbance and pH were taken at 1, 2 and 3 hours.

2.3.5 Acid Wastewaters

Kinleith acid

Experiment 5: Multiple doses of wastewater

Experiment 5 follows the same procedure as experiment 3 but uses Kinleith acid waste. 10 g of diatoms were used as the higher diatom mix amount. 6 g of diatoms were used for the lower mix amount.

6 and 10 g of diatoms initially stirred with 100 ml of wastewater. At 12, 24 and 38 hours stirring an additional 50 ml of wastewater were added until 250 ml of total wastewater. The solution was stirred for a total time of 50 hours.

Sample aliquots for absorbance and pH were taken every 2, 4, 6 and 12 hours from the start and after each 50 ml wastewater addition point.

Experiment 6: Rapid response

To look at the first 2 hours of stirring, the first sample was taken at 5 minutes and then every 10 minutes. In a second experiment set the first samples was taken at 30 seconds then every 10 seconds. To obtain absorbance and pH results quickly, centrifuging of the sample aliquots instead of a time settling method was used.

Acid wastewaters were centrifuged for 10 minutes at 3900 rpm, the supernatant was pipetted off, and 200 ml was mixed with 16 g of diatoms. The mixture was stirred magnetically as in previous mixes; test aliquots were collected at the set intervals with plastic disposable syringes. The stirring was continuous whilst collecting samples. The collected aliquots were centrifuged for 10 minutes at 3900 rpm, the supernatant pipetted off and absorbance and pH recorded.

2.3.6 Reclamation of Organic Surface Deposits and Diatoms

Reclamation of Organics

The 6 g diatoms stirred with 250 ml from stirring method 5, Kinleith acid wastewaters were centrifuged and the supernatant drawn off. The diatom slurry was magnetically stirred with 100 ml of 3 mol NaOH for 2 hours. The mix was filtered on a Buckner funnel through a GF-C filter whilst being washed with a further 100 ml of NaOH. Absorbance and pH were measured for the collected liquid.

Reclamation of Diatoms

The NaOH washed 6 g of diatoms (Reclamation of organics) was further washed with copious amounts of distilled water. The washed diatoms were then magnetically stirred with 100 ml of Kinleith acid waste for 2 hours. At 2 hours stirring a sample was taken and measured for pH and absorbance.

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Chapter 3

Results and Discussions

3.1 Introduction

This study started with a packed column filter, subsequent experiments followed by stirred mixes of diatoms and wastewaters to improve the accessibility of wastewater colour compounds to active diatom surface sites. Initially chloroplatinate units were used to express colour. However the standard method required buffering to control pH, which was found to drastically affect colour retention. Direct measurement of absorbance and pH was subsequently used. Data results are tabled in Appendix C.

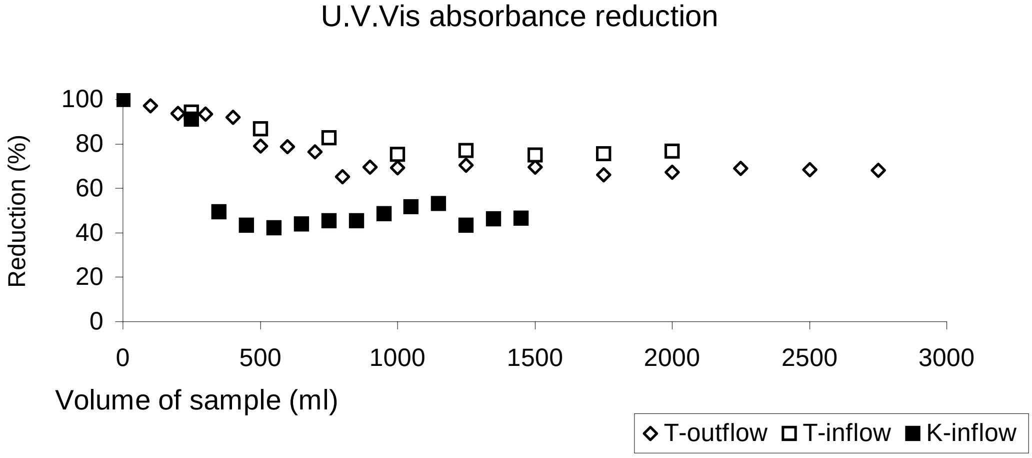
Sets of variables were initiated for filtering ability:

1- Upper and lower limits of diatom dosage to wastewater volume.
2- Upper and lower pH values for effective absorbance reduction.
3- Ideal mixing time to achieve the best filtering results at optimum dosage and pH values.

By ascertaining the limits of these variables proposals of mechanisms could be suggested.

3.2 Packed Column Filter

There was high initial colour removal, which decreased with the addition of more sample waters, graph 3.0.



Graph 3.0: *Percentage reduction in absorbance, packed column filter*

There was visible fractionation of the wastewaters in the form of fronts traveling down the column, compounds in the absorbance range of 300 to 350 nm eluting at a faster rate. The Kinleith pond inflows also flowed much faster and with less colour drop as measured by absorbance, table 3.0.

Time (minutes) taken to elute 250 ml aliquots:

Site	Starting aliquot	Final aliquot	Average flow rate
K-inflow	12	15	15
T-inflow	12	48	36
T-outflow	12	64	40

Table 3.0: *Packed column filter elution times*

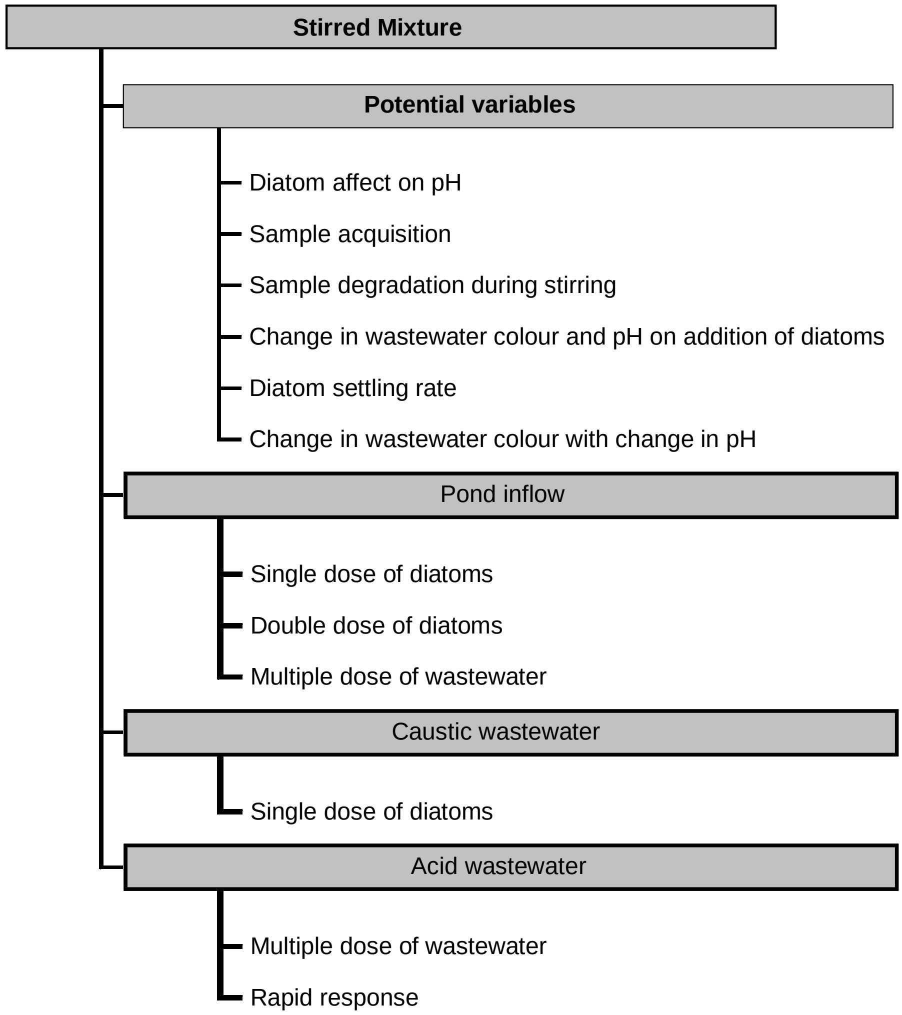
Volume of wet diatoms = 1590 (internal $r^2\pi$) x 42.5 (wet length average)

= 6760 mm^3

= 0.0676 L

3.3 Stirred Adsorption Studies

Experiment flow chart



Diatom Settling Rate

The presence of diatoms suspended in the distilled water was indicated by higher absorbance readings. At 10 hours settling time the absorbance difference between the stirred diatoms and the blank was $\pm$ 0.005, which is within the machine error limits. At 12 hours, settling appeared complete, with the difference between the sample and blank also $\pm$ 0.005.

There was no mud-line as expected by a flocculent type material (Rushton, Ward et al. 1996), a general reduction in clouding with a corresponding increase in sedimentation was observed as the diatoms settled. At 8 hours settle time a visible difference was noted between the cloudy diatom mix and the water, this was at 20 mm maximum above the settled diatom sediments, but not strictly a mud line. This clouding had disappeared by the 10-hour period.

Sample Degradation

At 12 hours the pond wastewater outflows showed a drop in absorbance of 12.7 % (average across measured frequencies). There was no measurable change in the pond inflows, caustic and acid wastewater samples.

Diatom effect on pH

After 6 hours of stirring all diatom water samples showed a pH of 3.77, table 3.1-diatom pH.

Diatoms (g)	Start pH	2 hours	4 hours	6 hours	12 hours
5	4.88	3.57	3.61	3.77	3.78
6	4.88	3.80	3.78	3.77	3.77
8	4.88	3.78	3.78	3.77	3.78

Table 3.1: *diatom pH (100 ml of distilled water)*

Although diatom frustules are amorphous or biogenic silica structures, the sediments used consist of whole and part diatoms. A considerable amount of active silanols could be present, organic silanols and siloxanes have been shown to be acidic in nature (Voronkov, Mileshkevich et al. 1978) and therefore the most probable cause of the pH change in the distilled water mixed with diatoms. Cation adsorption of calcium or sodium can lower pH, Calcium and sodium levels in the distilled water samples were below the limits of detection.

Change in wastewater colour with change in pH

Higher absorbance figures were observed at higher pH (Fig 3.1) which is consistent with other research (Diez, Mora et al. 1998; Wingate 2002). Although machine errors in absorbance and pH were both 5% the change in absorbance with pH was sufficient to explain results in later experiments.

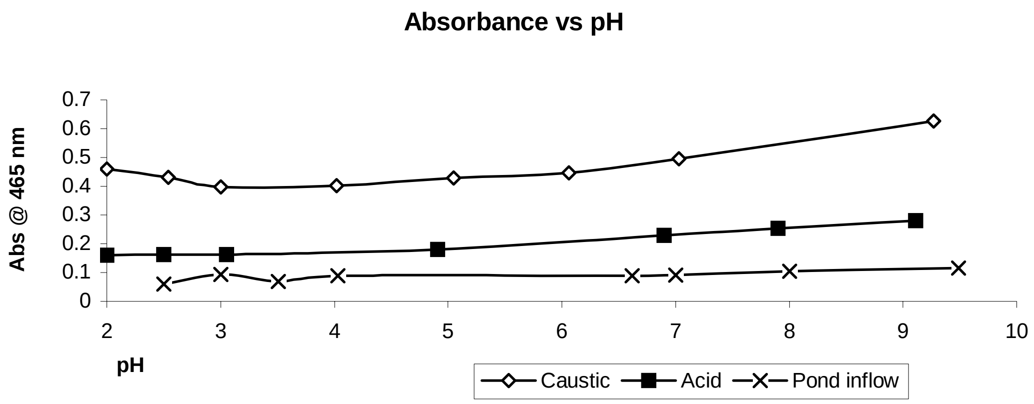


Figure 3.1: *The effect of pH on absorbance for the main wastewater streams.*

Change in wastewater pH and absorbance by addition of distilled water

The mix of wastewater with distilled water diluted the colour and balanced out the pH much as would be expected, table 3.2.

	350nm	PH
Distilled water	Blank	6.90
Bulk wastewater	0.460	7.76
100ml distilled water and 50ml waste	0.164	7.20

Table 3.2: *The effect on pH and absorbance of distilled water by the addition of wastewater.*

3.3.1 Neutral pH Wastewater

Tasman Mill, settling pond inflow (Tasman inflow)

Experiment 1a: Single dose of diatoms

A reduction in colour was achieved in all the experiments, at 4 % diatoms to sample waters (4 g diatom/100 ml sample). The best reduction in CPU occurred of 65 %, Fig 3.2. Visually the yellow colour associated with the wastewater decreased after 5 hours of stirring. The diatoms imparted a gray colour to the mixed solution; the gray colour settled out within 10 hours once stirring was stopped.

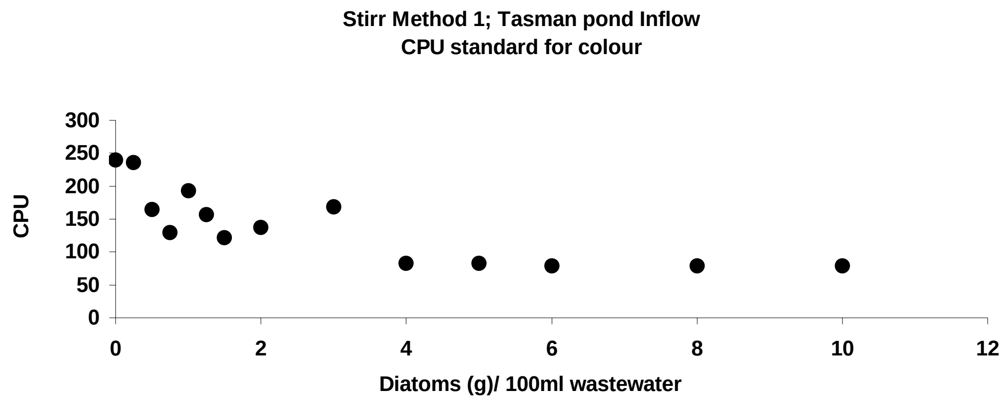


Figure 3.2: *Colour reduction as a function of the ratio of Tasman pond inflow water to diatoms*

From 5 % diatoms a white or milky clouding of the sample occurred during the buffering phase of the CPU standard, a phosphate formation, giving inaccurate absorbance readings. The clouding disappeared with very heavy buffering. The CPU standard used requires all absorbance readings to be taken at 465 nm; pH 7.5 $\pm$ 0.05 adjusted with HCL and NaOH/$KH_2PO_4.2H_2O$ solutions. Other researchers were noted as using 440 nm (Diez, Mora et al. 1998).

The clouding issue was also reported by SCION and Pulp Mill staff in personal communications (Hejl 2005; Slade and McGrouther 2005; Fulton 2006). This clouding could add inaccuracies to absorbance readings and with the calculating of dilution factors. As any system developed would hopefully have industrial applications, it was therefore decided not to buffer samples, but to measure sample pH concurrent with absorbance during the remainder of the stirring experiments.

Colour reduction was observed with all the diatom amounts used. The best results were obtained from the 4/5 g diatom per 100ml wastewater, this ratio was decided on as a minimum for the next series of experiments.

Experiment 1b: Single dose of diatoms

Absorbance readings reduced in the first 2 hours of stirring for 8 and 10 g of diatoms with 100 ml wastewater. Both mixes showing similar trends the 8 g mixture had slightly more initial absorbance reduction. The plots for the 5 and 6 g diatoms followed different trends than for the 8 and 10 g diatom mixes. The 5 g diatom mix showed higher absorbance readings than the others at the 2-hour stir time, dropping to a minimum at 12-hours, Fig 3.3. In the first 12-hours of stirring, the pH drops quickly, then stabilised for all mixes.

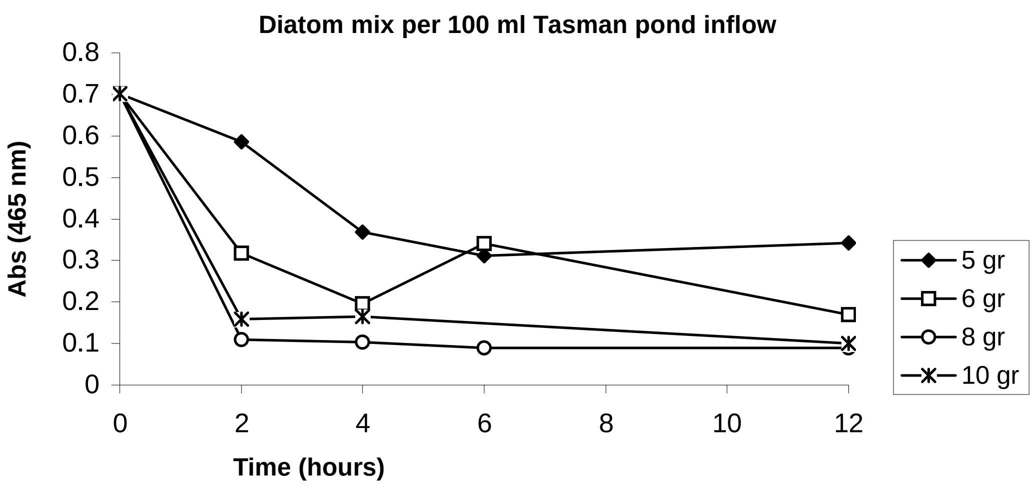


Fig 3.3: *Single dose of Diatoms- amounts of 5, 6, 8 and 10 g mixed with 100ml of Tasman pond inflow wastewaters in a stirred filter.*

Experiment 2: Double dose of diatoms

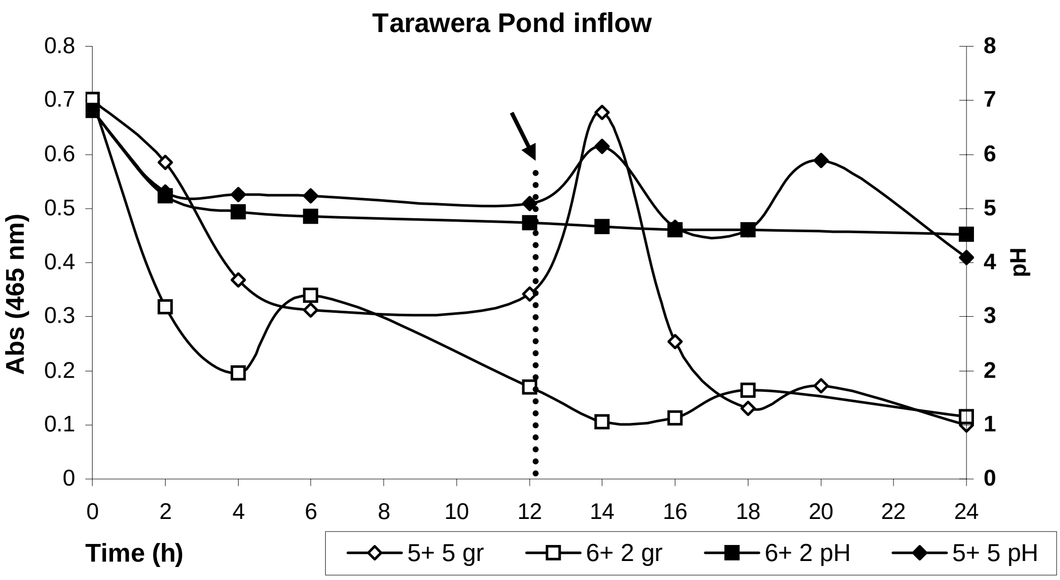


Figure 3.4: *Double dose of diatoms. 5 and 6 g diatoms mixed with 100ml of Tasman pond inflow wastewaters in a stirred filter. Zero to 12 hours is for 5g and 6g in 100ml of wastewater. At 12 hours (arrowed) 5g were added to the 5g mix and 2g to the 6 g mix, a further 15ml of wastewater was also added to top up the liquid level. The increased absorbance is largely due to clouding by diatoms.*

Figure 3.4 includes the data from fig 3.3, and continues to plot the 5 g sample with an additional 5 g of diatoms added at 12 hours. The 6 g sample had an additional 2 g of diatoms added at 12 hours. Absorbance and pH peaks were observed for the 5 g sample at the extra diatom addition point and occurred in both replicates, suggesting suspended diatom material affecting the results. There was a slow rise in absorbance for the 5 g mix from 6 to 12-hour suggesting that the peak (seen for 6 g at 6 hours, fig 3.3) may be at a later point (not tested for).

The 6 g diatom reduced absorbance until the 6-hour stir time when a rise in absorbance occurred, the absorbance then reducing to the low at 12-hours. 2 g of diatoms was added at 12-hours to make 8 g total plus 15 ml of wastewater. At 18-hours absorbance rose a second time, fig 3.4. The absorbance rise at 6 hours and at 18 hours (6 hours after addition point) may be due to similar effects. Studies

(Stumm 1992) have shown that coagulation and flocculation effects follow a regular pattern related to dosage and wastewater concentrations. Coagulation or flocculation at low concentrations can result in an initial reduction (colour, turbidity etc.) competing reactions can then displace the adsorbed material resulting in a rise in colour and turbidity. The initial colour drop a result of a sweep floc by diatom material activated by pH changes. Colour removal was then reversed as pH rises. The low dose rate was not able to sustain the lower pH needed for colour removal. Colour was reduced again as pH falls below the critical value of around 5.

There was reduction in absorbance for all of the diatom mixes used. Increasing the diatom amounts in the 5 and 6 g samples to 10 and 8 g respectively gave similar reductions in absorbance after 24 hour stirring as the 8 and 10 g mixes at 12 hours stir, fig 3.3 and 3.4. There was a large drop in absorbance within the first 2-hours of stirring. This is similar to results for allophane mixed with pulp mill wastewater (Dixit and Van Cappellen 2002). The dose rate of 8-10 g diatoms to 100ml wastewater had the most effective absorbance reduction, within the first 2 hours.

Experiment 3: Multiple doses of wastewater

Experiment 3 tested a fixed diatom amount with multiple doses of wastewater to ascertain a saturation point. As all mixes had similar end results for absorbance reduction at final mixes of 8 or 10 g, 8 and 10 g were chosen as the fixed diatom amounts to test for saturation.

The first 12-hours stir with 100 ml of wastewater returned similar results to the 8 & 10 g per 100 ml mixes in stir method 2, fig 3.3. The 8 g diatoms mix lowered absorbance faster than the 10 g mix. From the start of 50 ml wastewater additions, at 12 hours, the 10 g diatom mix gave lower absorbance and pH readings, fig 3.5 and 3.6.

Peaks for pH and absorbance at 12.5, 24.5 and 36.5 hours are from the 50 ml addition. A higher minimum pH was observed after 12 hours of stirring from the 50 ml addition points.

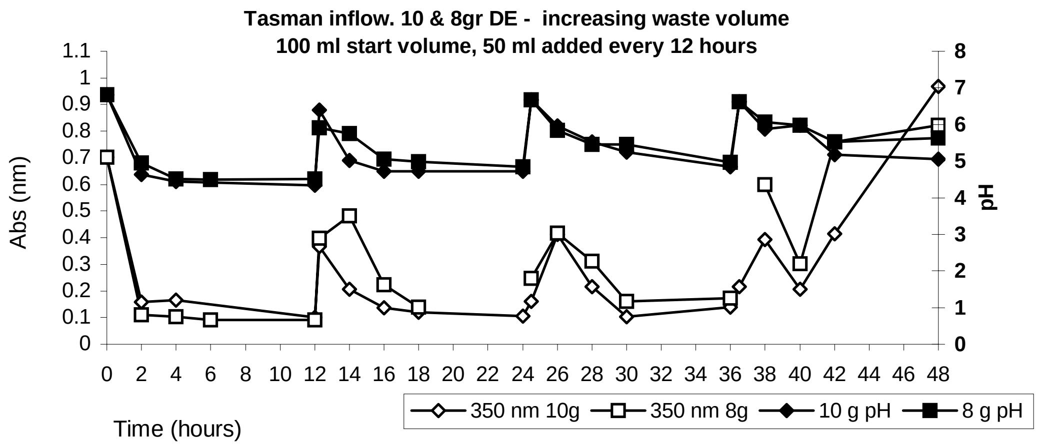


Figure 3.5: *The response of absorbance and pH to multiple doses of wastewater at 12-hour intervals. Experiment 3, for 8 & 10 g of diatoms*

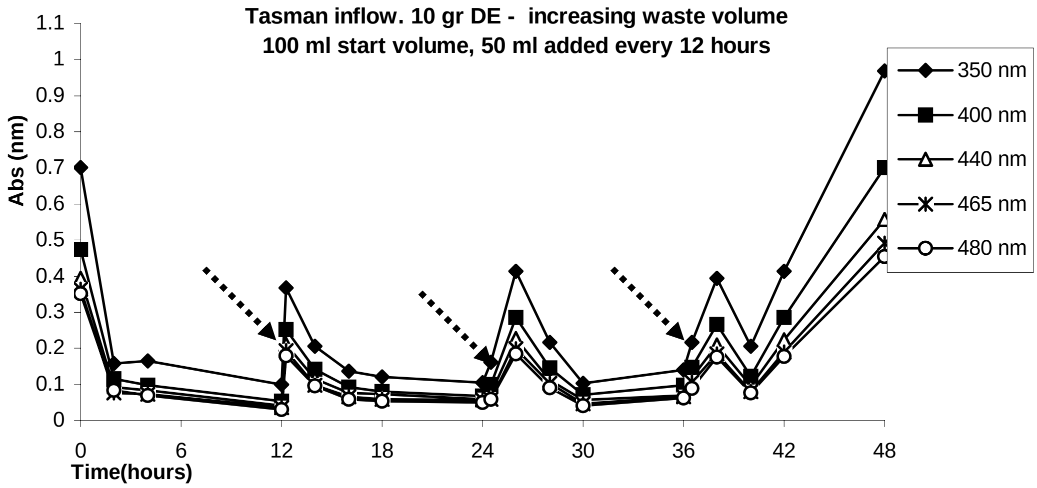


Figure 3.6: *The response of absorbance for several wavelengths to multiple doses of wastewater at 12-hour intervals. Experiment 3, the addition of 50ml aliquots of wastewater was at 12, 24 and 36 hours (arrows).*

Diatom amounts were fixed the starting ratio of 10 (10 g diatoms to 100 ml wastewater) becomes 6.6 (150 ml wastewater), 5 (200 ml wastewater) and 3.2 (250 ml wastewater). The collision rate of diatoms with waste must decrease. The diatoms may also be loosing their effectiveness due to saturation with waste affecting colour and colour removal and the removal of active surface sites.

An alternative explanation could be that the diatom adsorption of colour is at a very rapid rate, but pH dependant. The diatom pH buffering effect on the wastewater is slow so each addition of wastewater raises the pH, reducing the affects of adsorption. The diatoms slowly reduce the pH to a point where colour removal resumes.

At 40 hours a marked rise in absorbance to levels greater than the initial wastewater occurred, whilst pH dropped, fig 3.5 and 3.6. From the 40 hour point ‘saturation’ of the filtering abilities of the diatoms was reached for the conditions of the experiment.

At 40 hours stirring and all other points of high absorbance readings the pH was above 5. Studies with allophonic suspension-effluents gave the best colour removal at 5.0 pH as a result of the increasing positive charge on the allophonic compound, facilitating the reactions between the colour phenolic compounds and AL-OH and Fe-OH surface sites (Diez, Mora et al. 1998). The ICP MS results for zero, 24 and 48 hours stirred wastewater with diatoms showed no change in aluminium and iron concentrations, the Al (3% maximum) present in the diatoms, as part of the crystal structure may not have sufficient OH groups accessible to the organic colour to explain the large colour removal. Dissolution of the biogenic silica below a pH of 5 may therefore be driving absorbance and colour removal. The biogenic silica acting as a coagulant, forms flocs that are then removed by the remaining diatoms, reducing absorbance.

3.3.2 High pH wastewaters

Kinleith caustic, Tasman caustic and continuous digesters

Experiment 4: Single dose of diatoms

The Tasman Mill Continuous Digester sewers had an average pH of 9.1, and 10.6 for the caustic stream over the collection period (Fulton 2006). The Kinleith Mill caustic stream average for the collection period was pH 9.9, and the acid stream pH 4.7 (Hejl 2006).

Settling times for the diatoms in all the caustic solutions were longer than for the acid and neutral wastewaters, being greater than 15 hours. Grey clouding of the solution increased in the continuous digester (CD) sample with time, and as the pH rose, this clouding remained in the sample test tubes and blocked the GF-C filters. The same grey clouding was also apparent in the caustic sample, this may be from an initial release of material on the diatoms due to polarity changes from the higher starting pH.

	465 nm	pH	
Caustic	0.097	11.29	Start
	0.245	7.67	1 h
	0.192	7.66	2 h
CD	0.036	8.99	Start
	0.016	5.49	1 h
	0.033	5.85	2 h
	0.043	6.42	3 h

Table 3.3: *Initial Kinleith caustic and Tasman Mill continuous digester (CD) results*

CD 55 % reduction at 1 hour, 8 % reduction at 2 hour, 16 % increase at 3 hour.

Caustic 60 % increase at 1 hour, 50 % increase at 2 hours.

The low absorbance observed for the CD 1-hour sample (table 3.3) was close to the pH 5 limits and within the 2-hour active period seen in stir method 3, the absorbance rising as the pH rose. The absorbance change due solely to pH in the 5 to 7 pH range was around 13 %, with the absorbance rising with pH, fig 3.7.

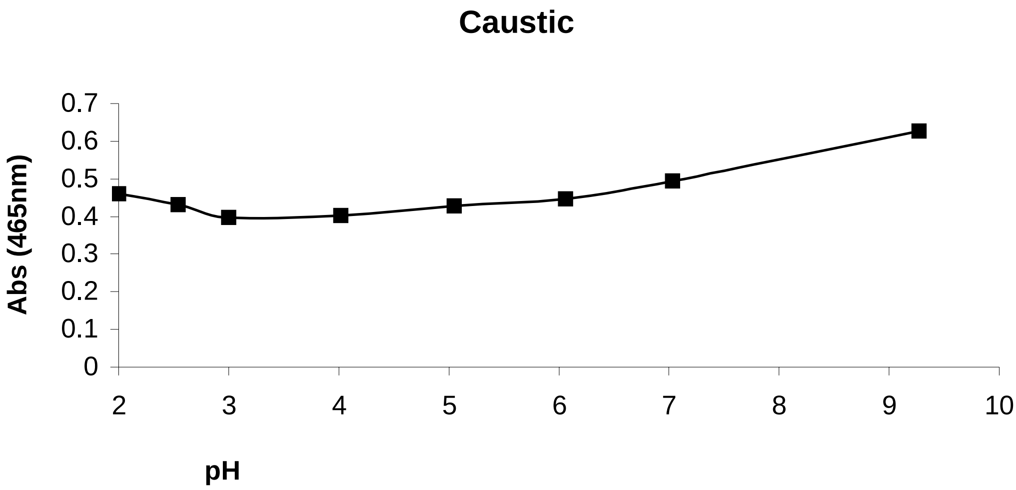


Figure 3.7: *Kinleith caustic wastewater absorbance at 465 nm, measured across a range of pH. The pH was altered using HCL and NaOH, data from graph 3.2.*

During this period discussion over results from the acid, caustic and neutral wastewater streams with contacts at Kinleith Mill (Mercer 2006) suggested that any applicable technology resulting from this work might best be applied to the acid stream. Further study on the caustic and CD wastewaters was stopped to allow work on the acid stream.

3.3.3 Acid wastewaters

Kinleith Acid

Experiment 5: Multiple doses of wastewater

The start pH of the acid wastewaters was 3.88. During these experimental mixes pH was never greater than 4, fig 3.8.

Over the first 12-hour stir the pH remained between constant (fig 3.8) at 3.70 to 3.96 for the 6 g mix and 3.62 to 3.94 for the 10 g mix. There was a drop to pH 3 after the first 50ml of wastewater addition, then a slow general rise in pH until 50 hours. The second addition at 26 hours caused the pH to rise slightly where as the additions at 14 and 40 hours caused ph to drop. The absorbance drops considerably within the first 2 hours of stirring and continues to drop during the first 12 hours, fig 3.9.

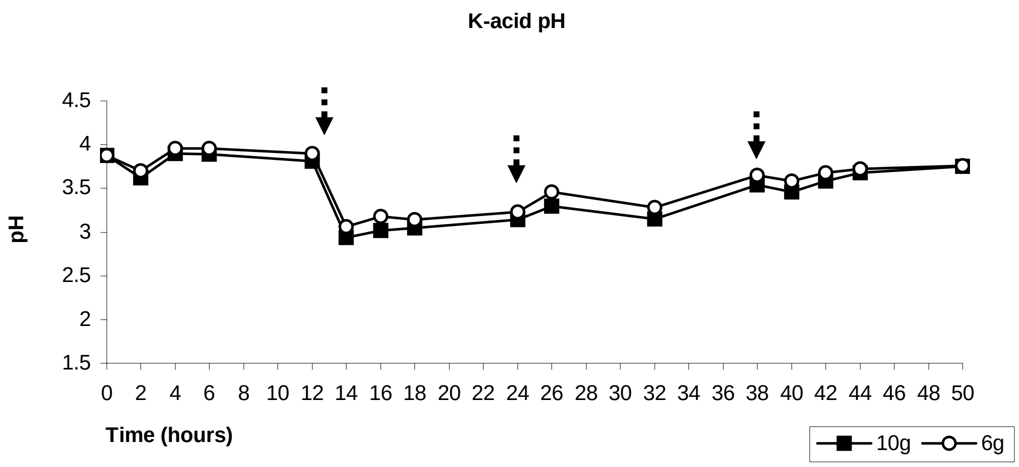


Figure 3.8: *The effects on pH of multiple additions of acid wastewater to a diatom suspension. Kinleith acid wastewaters, experiment 5, pH for 6 and 10g of diatoms. The initial wastewater volumes were 100ml. Additional 50ml wastewaters added at 12, 24 and 38 hours, marked with arrow.*

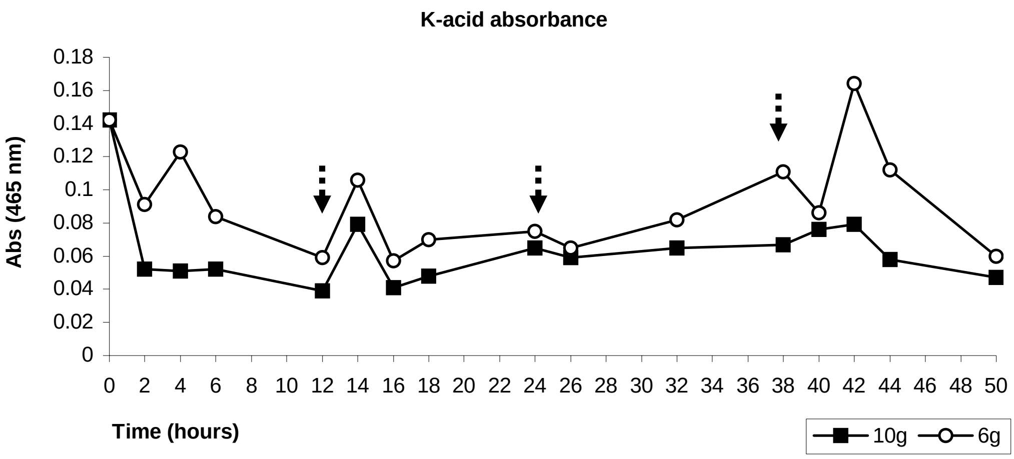


Figure 3.9: *Kinleith acid wastewaters, stirring method 5, absorbance for 6 and 10g of diatoms. The initial wastewater volumes were 100ml. Additional 50ml wastewaters added at 12, 24 and 38 hours, marked with arrow.*

The 50-hour absorbance reading of 0.047 nm was near the lowest readings obtained for 12 and 16 hours of 0.40 nm. There were some differences between the 6 and 10 g absorbance's, with the 6 g mix having rises at 4, 18 and 38 hours, corresponding to 4, 4 and 6 hours after the wastewater additions, fig 3.10. This may be due to the 6 g mix having diatom to wastewater ratios at the lower limits, similar to the pond inflow results, and therefore not a pH dependant effect. The peak at 42 hours was above the wastewater start absorbance but reduced to the 0.060 nm minima at 50 hours.

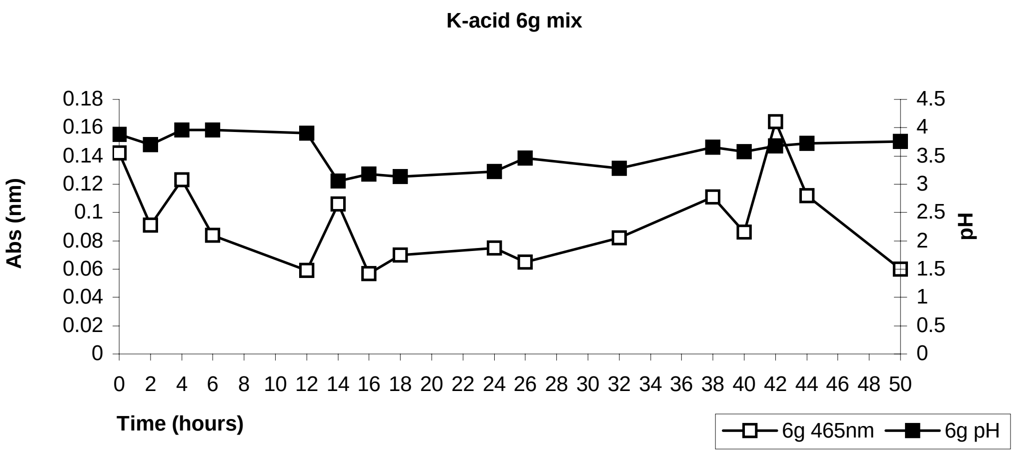


Figure 3.10: *Kinleith acid wastewaters, stirring method 5, absorbance and pH for the 6g mix.*

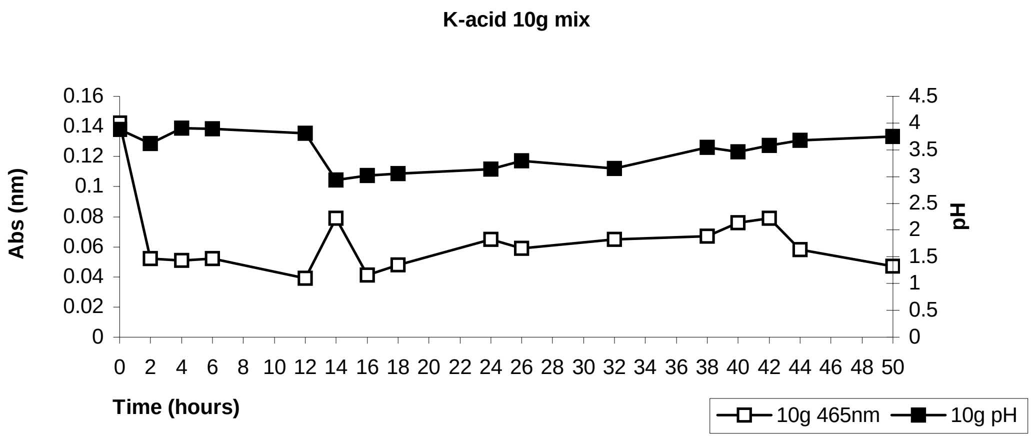


Figure 3.11: *Kinleith acid wastewaters, stirring method 5, absorbance and pH for the 10g mix.*

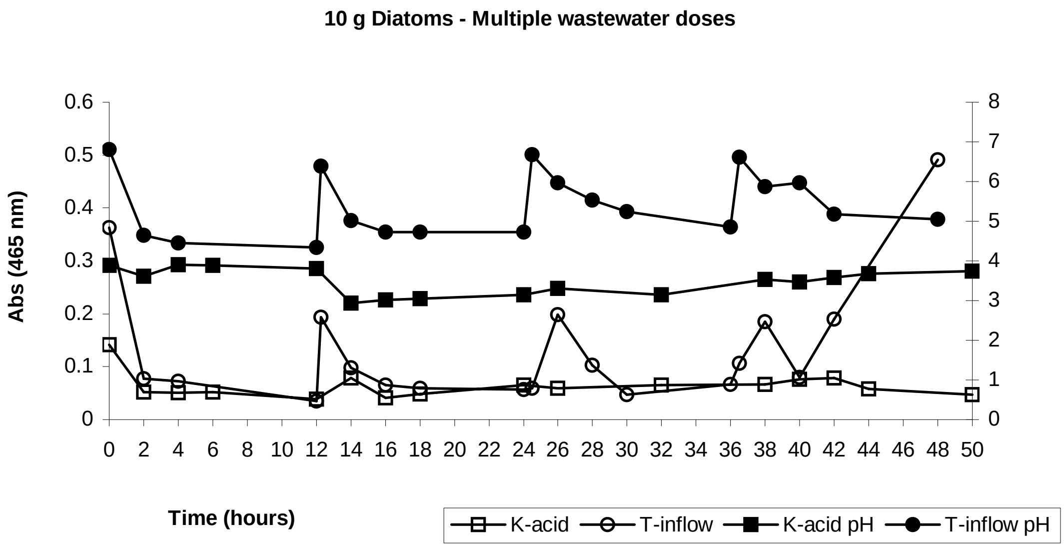


Figure 3.12: *10 g diatom mix experiments 3 and 5, absorbance (open symbols) and pH (closed symbols).*

In fig 3.12 Tasman inflow and Kinleith acid absorbance (465 nm) and pH results are compared. At the end of each 12-hour stirring section similar absorbance minima were shown for both wastewater flows. The best colour reduction happened within a pH range of 3.6 to 4.

Replicates were not run for two mixes in experiment 5. The similarities results in the 6 g and 10 g mixes for pH (fig 3.8) and absorbance (fig 3.9) suggest that the low 50-hour absorbance readings are not errors.

By adjusting the pH of acid wastewaters, absorbance was observed to drop with pH, fig 3.13. In the pH range of 3.6 to 4.0 this change is not substantial enough to explain the observed absorbance changes in acid mixed with diatoms. The lowest pH observed at 3.02 was lower than the acid wastewaters, pH 3.88, or the effect of diatoms on distilled water, pH 3.78. From ICP-MS analysis an increase in Al, Fe and Ca was observed. Al^{+3} and Fe^{+3} metal ions are strongly acidic, precipitating as metal hydroxides at low pH (greater than 4) and can adsorb on silica with the formation of acidic groups (Iler 1971). Dissolution of the biogenic silica and changes in surface charge below a pH of 5 (Dixit and Van Cappellen 2002) would allow the release of Al and Fe; this may explain the low pH.

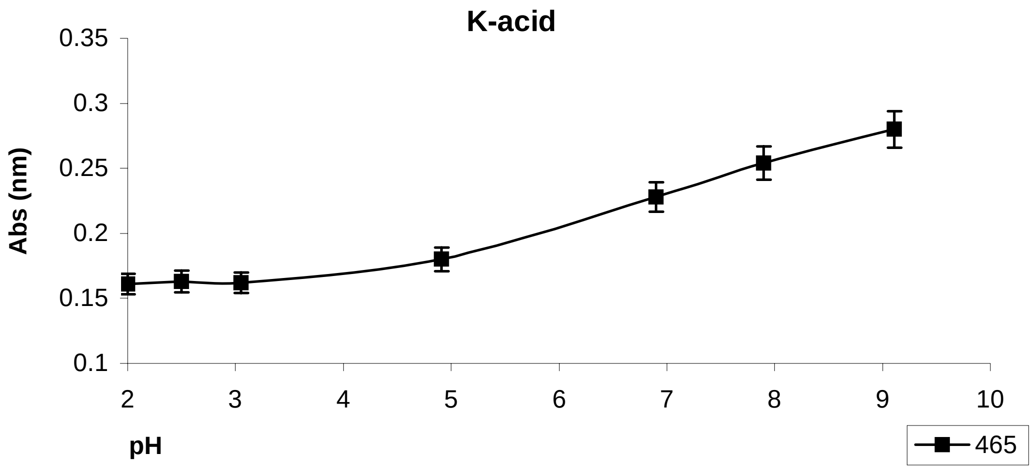


Figure 3.13: *Kinleith acid waste absorbance at 465 nm, measured across a range of pH. The pH was altered using HCL and NaOH as per section 3 and graph 4.1.*

Diatom Dosage Rate

A basic dosage rate is the percentage of diatoms to wastewaters. Efficiency of extraction will be determined by the dosage rate and reaction. The reaction time will control the contact time for the wastewater and diatoms within the stirred mixture. A rapid reduction in absorbance occurred within 2 hours, this is similar to results with allophane and pulp wastewater stirred suspensions, allophane reducing absorbance within 5 minutes (Diez, Mora et al. 1998). Investigations into the rapid rate potential of the diatoms follows in the next experiment set.

3.3.4 Rapid response adsorption studies

Experiment 6: Rapid response

Two stirring mixes were run. In one mixture a sample was taken at 5 minutes and then every 10 minutes up to 120 minutes. It was observed that a large reduction in absorbance occurred in the first five minutes of stirring. A second mix was prepared, a sample taken at 30 seconds and then in 1-minute intervals up to 10 minutes. Both stir mixes were run twice. With the method employed it was impractical to obtain samples earlier than at 30 seconds from the stirring start time.

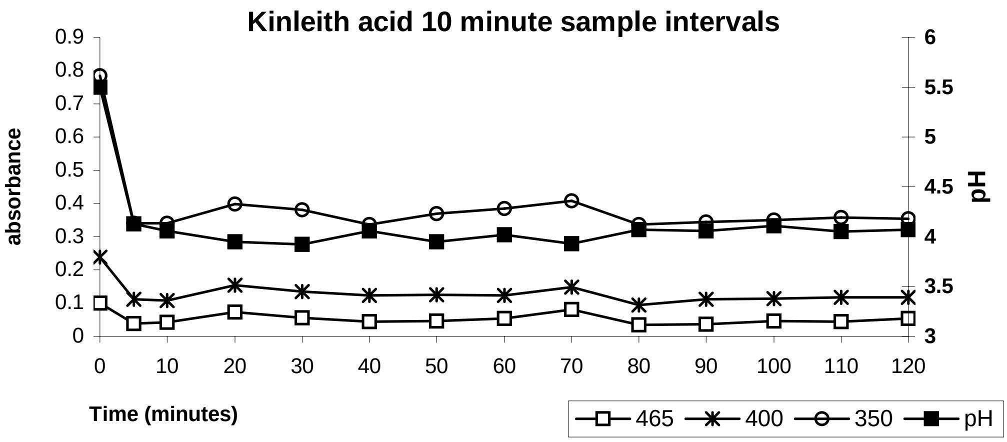


Figure 3.14: *Kinleith acid wastewaters experiment 6. Absorbance results for samples taken at 10-minute intervals.*

From fig 3.14 in can be seen that most of the absorbance reduction occurred within the first 5 minutes. Variations in the absorbance from 10 minutes until the end of the experiment mirrored changes in pH. The trend (not shown) for absorbance and pH was a slow drop over the 10 to 120 minute period

For the 0.5 to 10 minute stirring time, fig 3.15, the main absorbance reduction occurred within the first 0.5 minutes. As with the 10 to 120 minute stir experiment the trend for absorbance and pH (not shown) was a slow drop over the 0.5 to 10 minute period. The observed absorbance changes after the large initial drop in absorbance at 30 seconds were small enough to be the result of pH changes only. The data from fig 3.12 is plotted in fig 3.16 to better represent the pH verses absorbance variability.

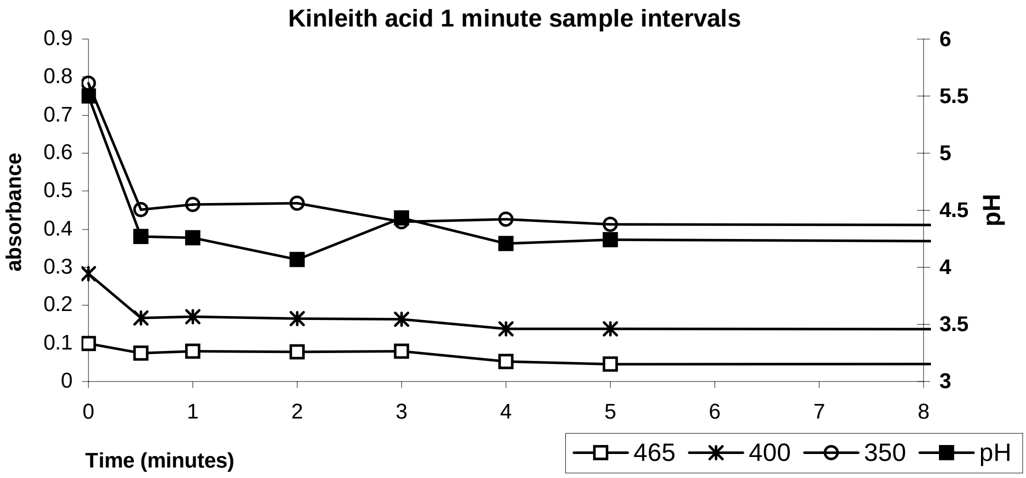


Figure 3.15: *Kinleith acid wastewaters stirring method 5. Absorbance results for samples taken at 1-minute intervals*

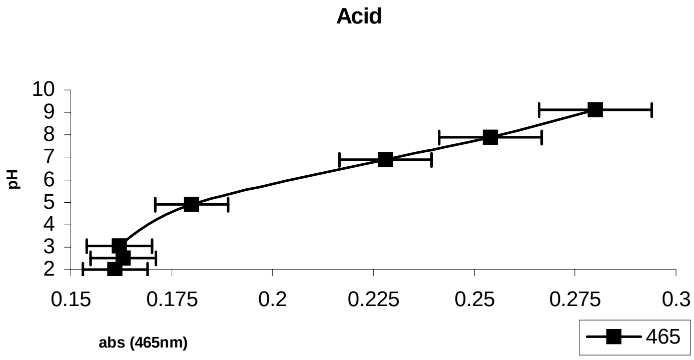


Figure 3.16: *Kinleith acid waste absorbance at 465 nm, this is the same data as in graph 3.14. The errors in absorbance and pH are both 5%.*

The supernatant from centrifuged samples were analysed by ICP MS. Concentration rises were observed in Al, Fe and Ca, with a drop in K concentration, fig 3.17.

Figure 3.18 shows similar results for the 10-minute sample mix with a continual slow rise in Al, Fe and Ca. Decreases in K and increases in Al, Fe and Ca indicate cation exchange was taking place, similar to that observed in experiment 5.

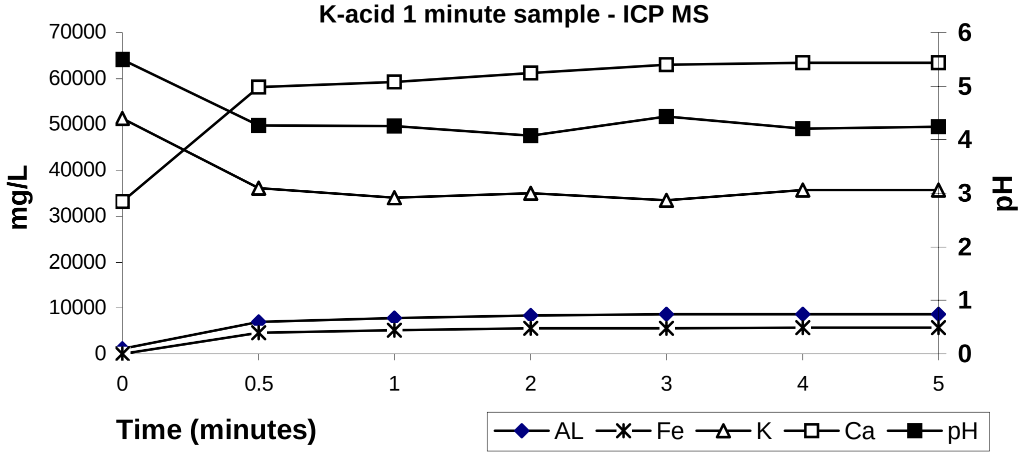


Figure 3.17: *Kinleith acid wastewaters experiment 6. ICP MS results for samples taken at 1-minute intervals.*

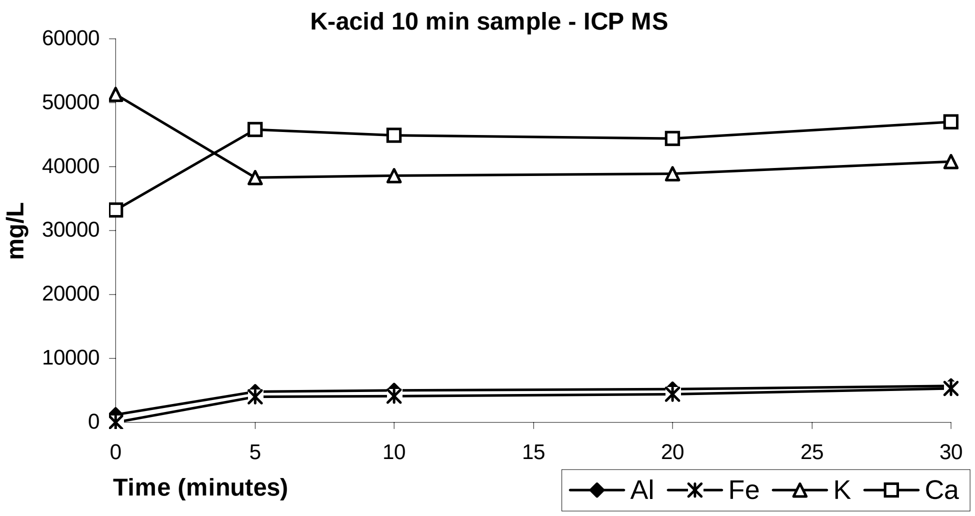


Figure 3.18: *Kinleith acid wastewaters experiment 6. ICP MS results for samples taken at 10-minute intervals.*

Absorbance (nm)	**465**	**400**	**350**
K-acid wastewater from bulk supply	0.189	0.418	1.033
Centrifuged	0.146	0.365	0.965
% Reduction from centrifuge	22.75	12.68	6.58
Centrifuged and filtered	0.100	0.283	0.784
% Reduction from centrifuge and filter	47.10	32.30	24.10

Table 3.4: *Reduction in the K-acid wastewater blank absorbance due to centrifuging alone, then centrifuging followed by filtering.*

The absorbance's graphed at zero time for stirring method 6, are for the wastewaters after centrifuging and filtering. Centrifuging and filtering reduced the absorbance from the initial sample bulk absorbance readings, detailed in table 3.4.

The majority of the materials in the wastewaters were organic. The fast reaction times and the general pH conditions in the stirred mix suggest organic H bonding to OH groups on silanols and siloxanes on the diatoms and in solution (Voronkov, Mileshkevich et al. 1978).

3.3.5 Reclamation of Organic Surface Deposits and Diatoms

When mixing diatoms in the caustic wastewaters an increase in colour was observed. The higher pH in the wastewaters could have affected the polarity of the diatoms allowing the release of material as opposed to adsorbing. NaOH was used to raise ph, as this was readily available with in Kinleith mill, the mill having the facilities to produce and reuse NaOH.

Reclamation of Organics

Washing of the magnetically stirred diatom mix with NaOH raised the pH to 11.57 resulted in a dark liquid. The dark liquid was diluted 3:1 with distilled water to obtain absorbance readings of 1.845 at 350 nm, 1.063 at 400 nm and 0.418 at 465 nm.

This was a preliminary experiment to assess whether the diatoms could be backwashed. The next step would be refining the process to ascertain the minimum concentration of NaOH necessary to release the organics.

Reclamation of Diatoms

Diatoms that had been washed with NaOH to reclaim organics were washed with copious amounts of distilled water, and then mixed with 100 ml of Kinleith acid wastewater.

After 2 hours of stirring a reduction in absorbance of 39.7 % for 350 nm, 30.8 % for 400 nm and 12.9 % for 465 nm was observed, table 3.5. The absorbance reductions for this experiment were not high and are similar to the reduction in absorbance by centrifuging and filtering 47% for 350 nm, 32% for 400 nm and 24% for 465 nm. The pH of the wastewater was 4.4 at the start rising to 5.36 after 2 hours magnetic stirring with the diatoms. The high pH was most probably a result of inadequate washing to remove NaOH.

Absorbance (nm)	**350**	**400**	**465**	**pH**
K-Acid wastewater from bulk supply	0.85	0.357	0.162	4.4
6g diatoms 2 hours stirred with K-acid	0.512	0.247	0.141	5.36
% Reduction in absorbance	39.76	30.81	12.96	

Table3.5: *Absorbance for Kinleith acid, 100 ml wastewater with 6 g regenerated diatoms*

Calcination of Diatoms

Diatoms from the reclamation of organics and from the Tasman inflow and Kinleith acid adsorbance experiments were washed with copious amounts of distilled water and then heated for 4 hours at 900^0 C. 6 g of diatoms were mixed with 100 ml of Kinleith acid and Tasman inflow wastewaters.

Diatoms mixed with the Kinleith acid wastewaters remained in suspension after centrifuging and filtering affecting the absorbance results. The pH of the wastewaters was not affected by the addition of the diatoms. The results for the diatoms mixed with Tasman pond inflows are in table 3.6.

Absorbance (nm)	Start	2-hours stirring
468	0.127	0.116
465	0.143	0.1215
440	0.165	0.150
400	0.210	0.197
350	0.384	0.344
pH	6.84	7.46

Table 3.6: *Absorbance for Tasman inflow, 100 ml of wastewater with 6g of calcinated diatoms*

3.3.6 SEM/EDS

SEM imaging was undertaken to provide a general image of the diatomaceous ooze and to ascertain if the nature of the adsorbed material could be determined. Used diatoms were compared to fresh diatoms.

Diatom morphology

A range of diatom types was found; the main types (by general shape not species) are pictured in images 3.1 to 3.5.

The dominant diatom type was identified as *Aulacoseira* (Thwaites 1948). Originally placed in *Melosira* (Thomasson 1974; Vinyard 1979; Cassie 1984; Round, Crawford et al. 1990). In excess of 99% of the sample diatom material was *Aulacoseira*. Similar figures have been obtained by M. Edwards for lake Rotorua (Edwards In print).

The following images are a selection representative of the many diatom types found in the L. Rotorua samples. The scale is at the bottom right of each image, magnification amounts are general, with no allowance for printed image sizing.

***Aulacoseira* Dimensions**

Averaged dimensions were taken from a large sampling of *Aulacoseira*. The separation valve to girdle bands were 14 μm in length x 10 μm diameter. The frustules had pore diameters of approximately 200 nm, with the pore inner mesh structure made from 5 or more holes in a sieve type structure, image 3.8, 9 and 11. The hymen had holes with a maximum diameter of 100 nm, image 1.1 and 3.10. The hypovalve and epivalve appear to have an inner layer similar to the outer hymen skin (image 1.4).

Chemical Composition

From EDS spectra of *Aulacoseira* diatoms, concentrations of Al < 1 to 3 %; Si, 86 to 92 %; O, 5 to 11 % with Fe, Na, K and Ca < 1 %.

The ICP-MS laser ablation data included diatoms, tephras, soils etc as opposed to EDX analysis of diatoms only. The sediments were not purified further than the wash and dry outlined for filter experiment 3 and are therefore indicative of the general diatomaceous ooze chemical composition. The aluminium concentration was 1% with Fe, Na and K all 0.1% at 1 - 2 mgL^{-1}. Calcium was at background levels of detection for the method used.

IR spectra

IR spectra of raw diatom samples had a strong narrow peak, at 467 cm^{-1} corresponding to Si-O(Si) symmetric vibrations (ν_s). There was a strong peak at 1090 cm^{-1} for antisymmetric vibrations (ν_{as}), this shorter wavelength corresponding to less strained cyclotetrasiloxanes and eight membered cyclocarbosiloxanes (Voronkov, Mileshkevich et al. 1978).

A wide strong peak was observed at 3440 cm^{-1} with smaller narrow peaks from 3670 to 3820 cm^{-1}. Peaks in the 3670 to 3820 cm^{-1} range are indicative of stretching vibrations in silanol OH (ν_{OH}) groups, concentrated groups or crystals have ν_{OH} shifts in the 3200-3300 cm^{-1} region. This absorption band of the silanol groups, bonded by the hydrogen bond, is characterized by width and intensity. Further shifts of 200-400 cm^{-1} from 3200-3300 are due to association and the high acidity of the silanols to carbinols (Voronkov, Mileshkevich et al. 1978).

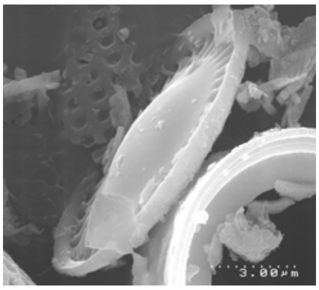


Image 3.1:

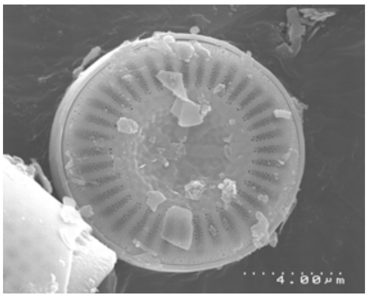


Image 3.2:

Image 3.3:

Round *Cyclottela* type diatoms images 1.2 and 3.

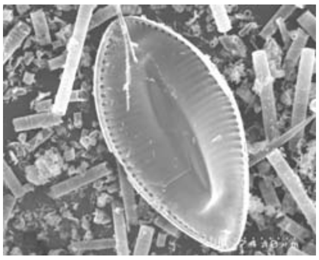


Image 3.4

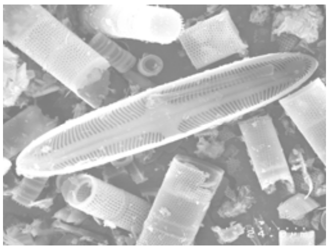


Image 3.5

Image 3.4 and 3.5 show larger diatom types.

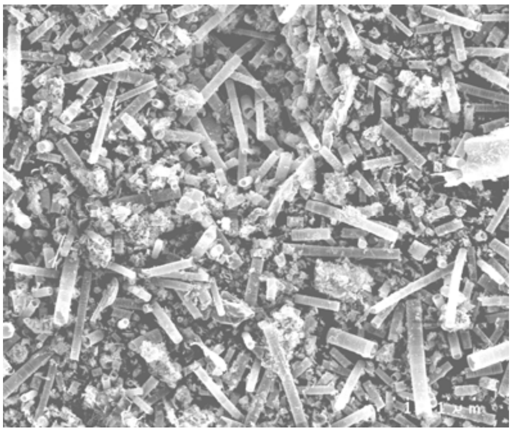


Image 3.6:
General SEM image of sediments
(500 x magnification)

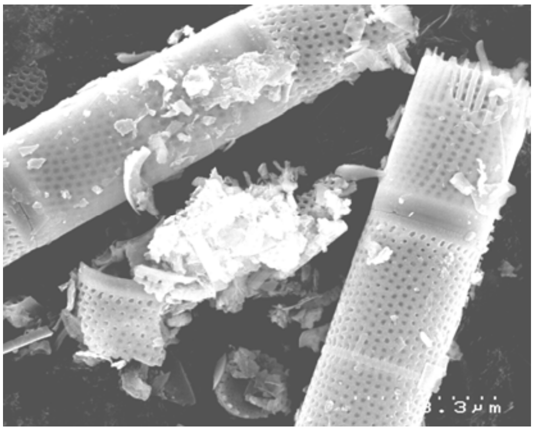


Image 3.7:
Aulacoseira; the main diatom type

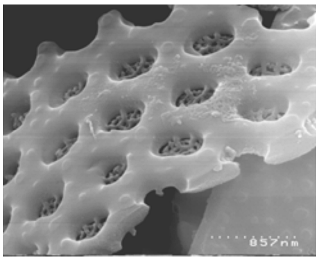


Image 3.8

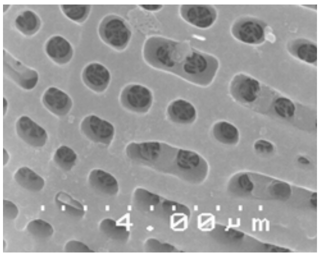


Image pore 3.9

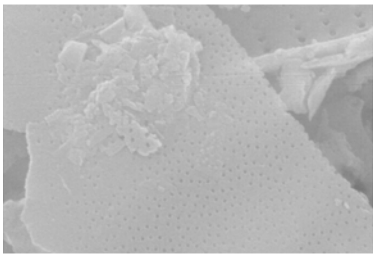


Image 3.10: Outer casing (hymen)

Pores (areolae) and internal pore structure
Image 3.8: scale: 874 nm.
70k x magnification
Image 3.9: scale: 4.00 μm
1.5K x magnification

Scale: 1.50 μm
45K x magnification.

(Aulacoseira)

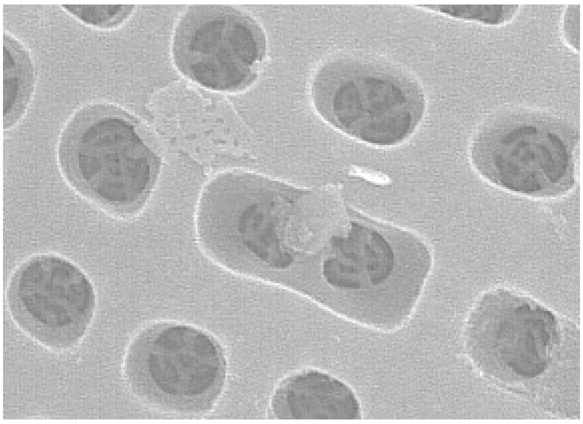


Image 3.11:
Aulacoseira inner pore sieve type structure (volate occlusions)
Close up of SEM image pore 3.9. The pores have an average diameter of 200 nm.

Adsorption Study Images

Counting of aggregate clusters in transects across SEM slides of diatom samples showed a 10 times increase in aggregates or conglomerates and a general increase in the size of the conglomerates compared to raw diatom samples, table 3.6, image 3.15 and 3.16. The term aggregates is used, as flocculation may not be correct

Transect block number	1	2	3	4	5	6	7	8
Raw diatoms	2	1	none	3	2	1	1	1
T-inflow 50 hours stirring	12	11	full	11	11	full	8	12
K-acid 50 hours Stirring	8	4	full	full	10	full	6	7

Table 3.6: *Transect block count for aggregates. Transect block size was 70 x 60 μm. Full = block all one aggregate, none = no aggregates in block.*

In most of the aggregates no center of attraction could be ascertained, the silicon and oxygen peaks swamped out any EDS signal that could indicate higher organic levels as a measure of colour based compounds. Where pulp fibre was visible there were often aggregates of diatoms around the fibre, image 3.13 and 3.14.

On close inspection of diatoms, separate and in aggregates, material coated on the surface and in the pores were noted, images 3.17, 3.19, 3.20 and 3.21. These surface coatings were only found in diatom samples from the end of the multiple wastewater addition experiments. EDS scans of the coating showed an increase in carbon content, suggestive of organic material, fig 3.21.

Very noticeable in hymen sections of diatoms was an effect similar to dissolution with fissures appearing in the structure, image 3.15, and a general mottling of the hymen surface. The fissures were also apparent on the edges of some main frustules structures. The main structures also appeared to have some mottling or surface roughness, images 3.20 and 3.22 compared to raw diatoms in images 1.2 or 3.8.

EDS scans were taken at many points during the SEM investigation of the diatoms. Pulp fibers had high carbon peaks, whereas the conglomerates and surface deposits always had high silica readings.

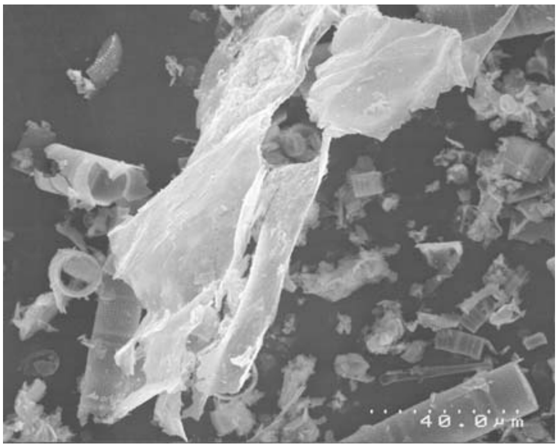


Image 3.12

Diatoms, diatom parts and a piece of pulp waste (large central sheet type object)
Scale (lower right) is 40 µm
(1500 x magnification).
Note many of the diatoms and diatom pieces are smaller than 40 µm.

(Aulacoseira)

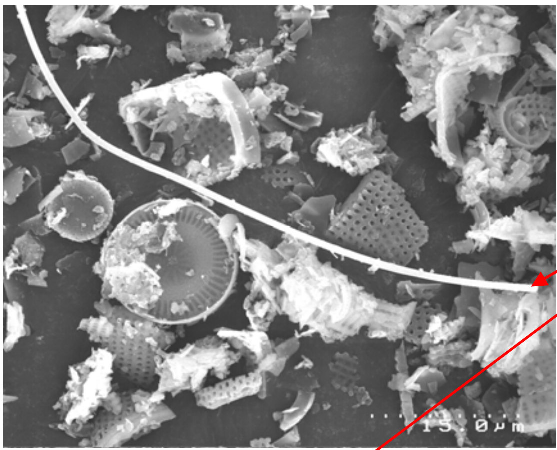


Image 3.13:

Pulp fibre - Single strand object

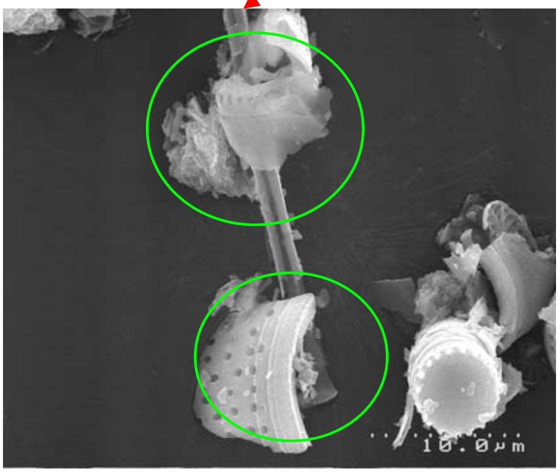
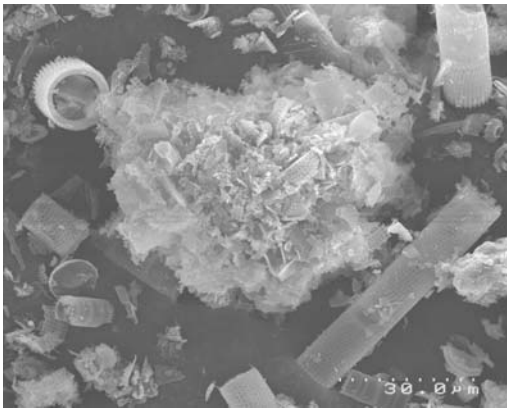


Image 3.14:

Aggregates around fibre circled in green



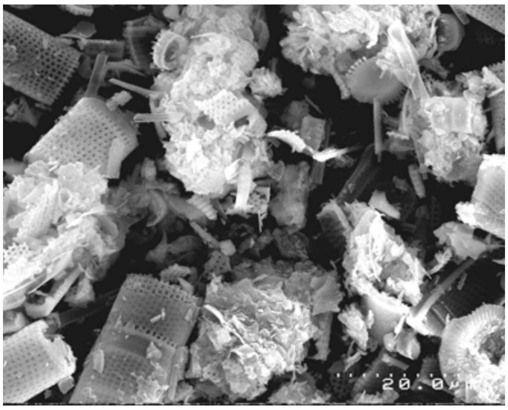


Image 3.15: *aggregates*

Image 3.16: *diatoms from 48 hours stirring showing aggregate groups*

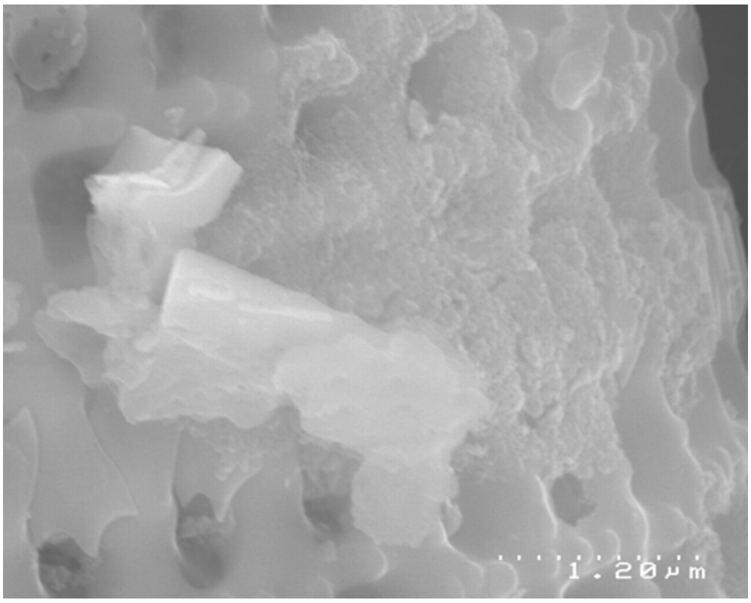


Image 3.17: *Surface deposits*

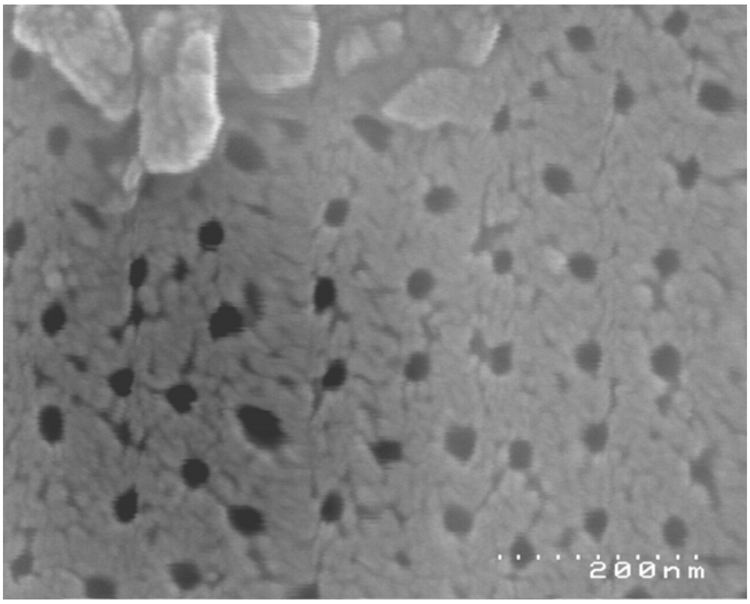


Image 3.18: *Hymen dissolution*

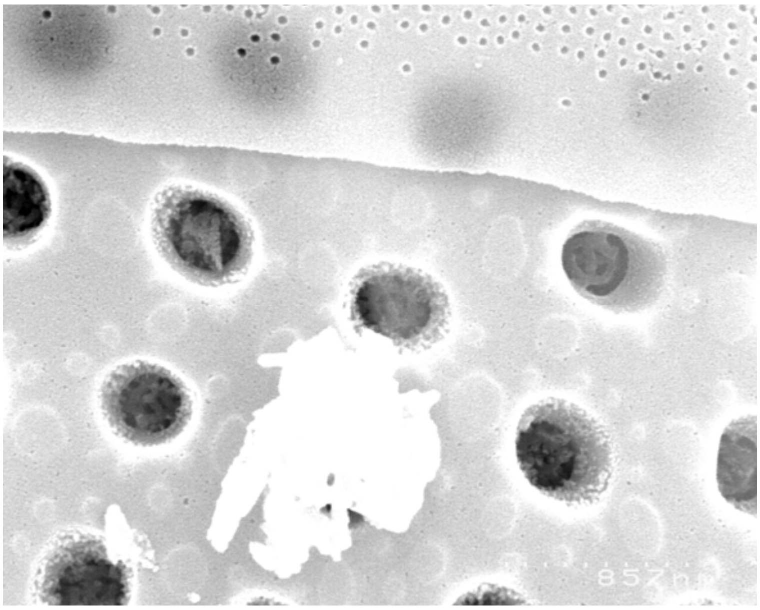


Image 3.19: *Hypovalve and Hymen, deposits forming within the pore structures*

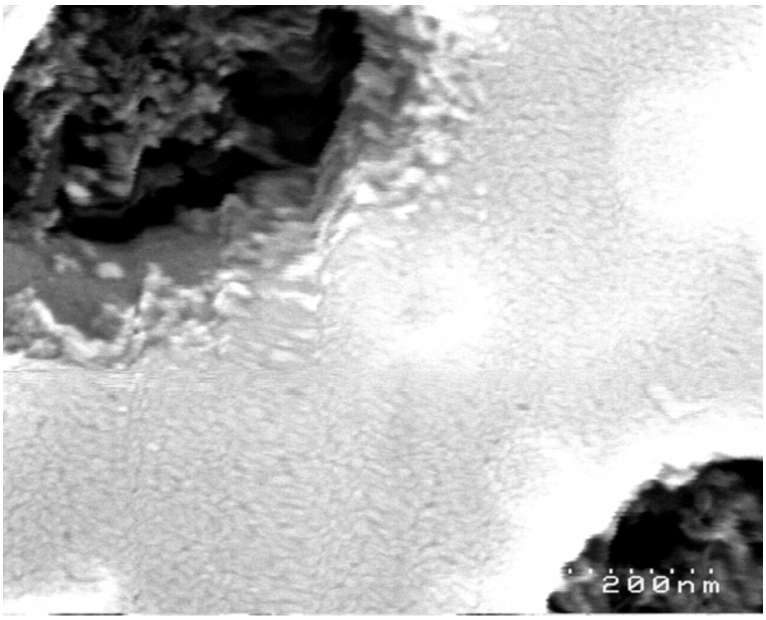


Image 3.20: *organic deposits within pores and surface mottling*

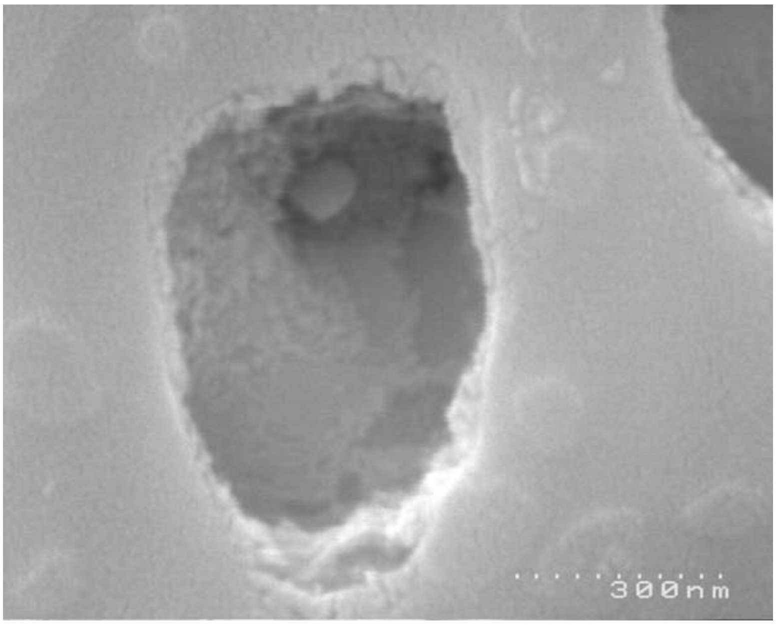


Image 3.21: *Deposits in pores and mild surface mottling*

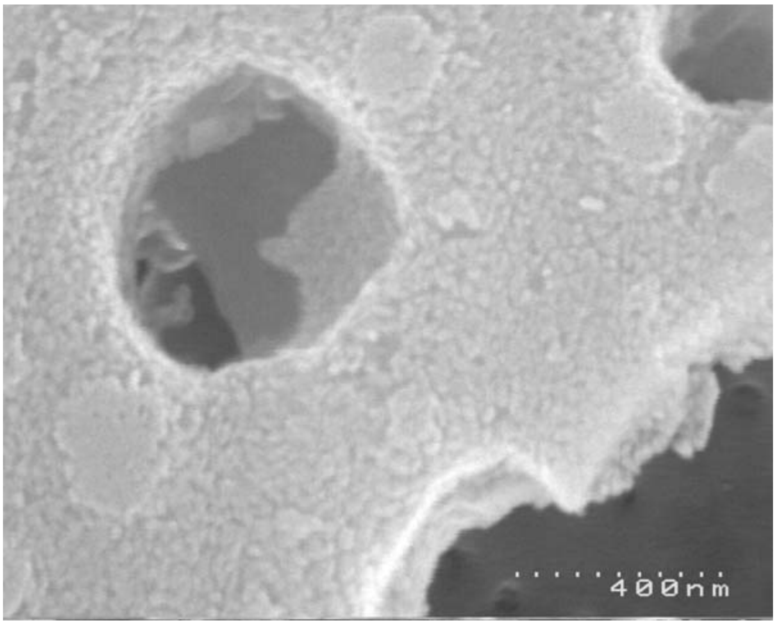
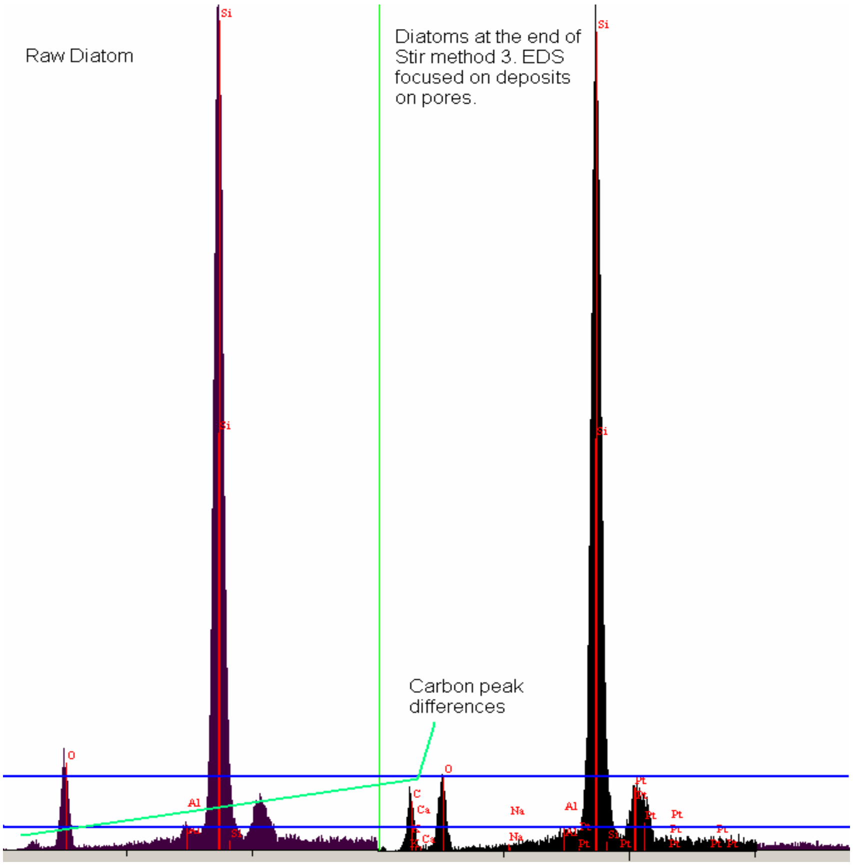


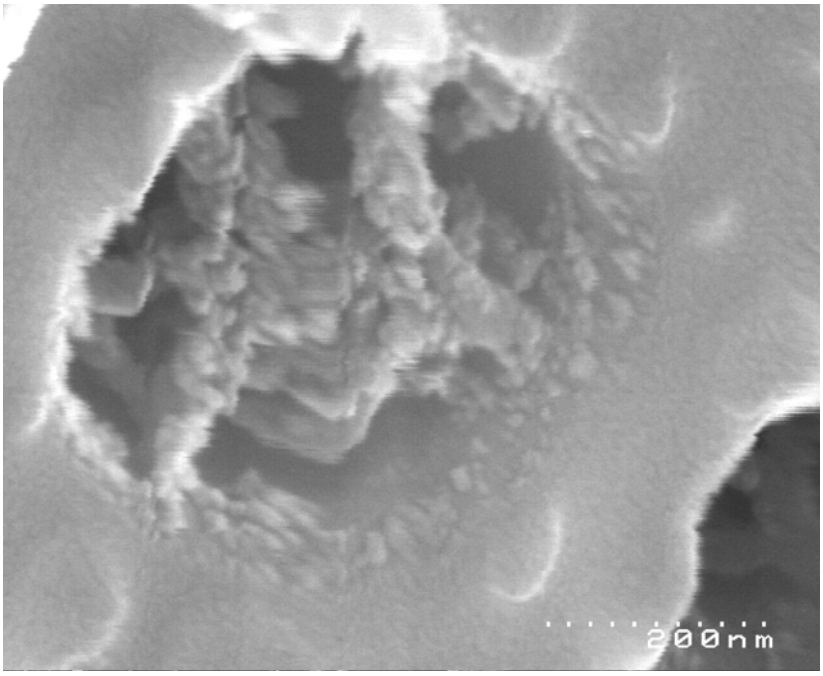
Image 3.22: *diatom surface mottling or dissolution*



I. EDS

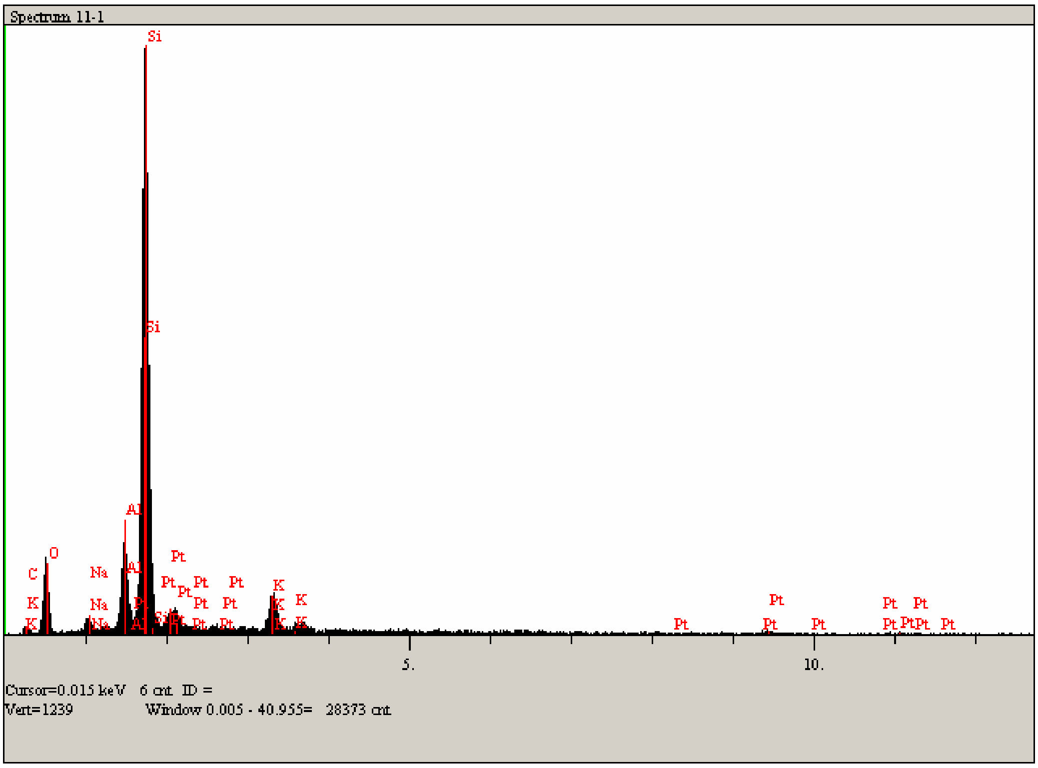
Oxygen

Aluminium

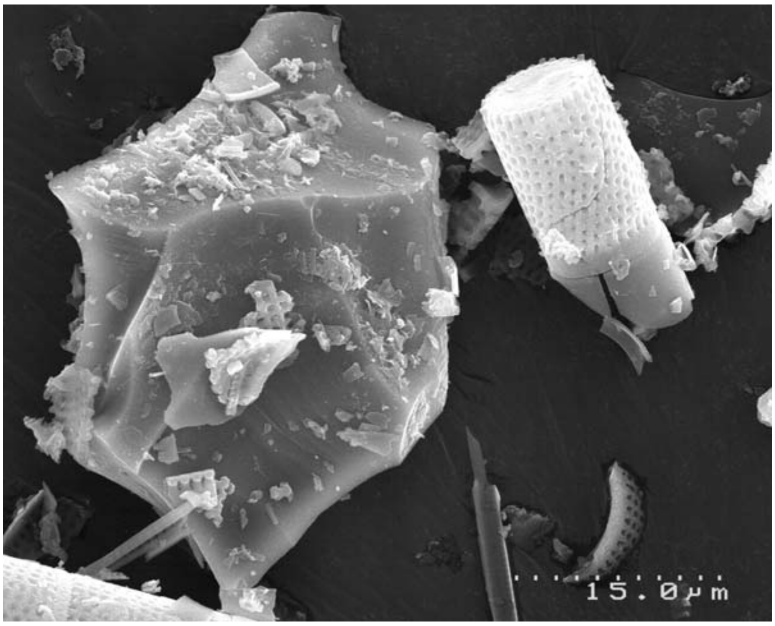


II. SEM

Figure 3.19: I, *EDS spectra of raw diatoms and deposits in the pores of diatoms used in the Tasman pond inflow stirred filter:* **II,** *SEM image of deposit for right-hand EDS spectra* **I.**

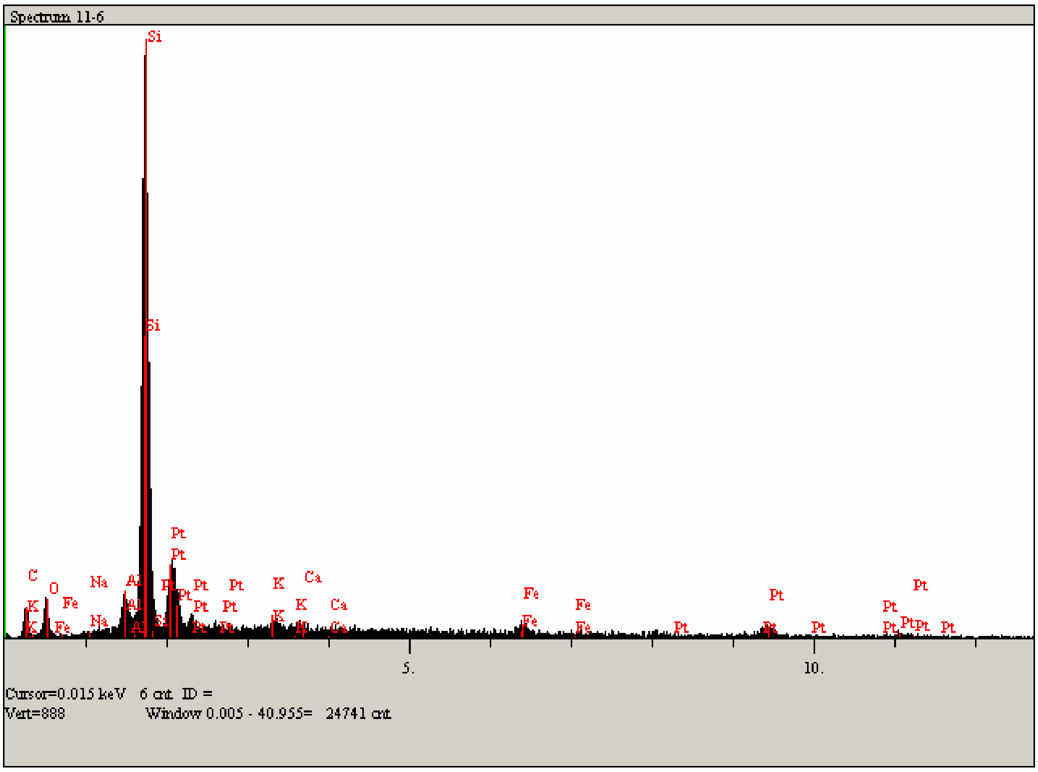


I. EDS of tephra glass shard (kV 20.0, Takeoff Angle 30.0°, Elapsed Livetime 100.0)



II. SEM image of tephra glass shard

Figure 3.20: *EDS* [I] *and SEM* **[II]** *of tephra from the diatom mix*



I. EDS of tephra (kV 20.0, Takeoff Angle 30.0°, Elapsed Livetime 100.0)

II. SEM of tephra

Figure 3.21: *EDS* [I] *and SEM* **[II]** *of tephra from the diatom mix*

The image and plots in fig 3.19 show the high silica peaks. Aluminium peaks were small; aluminium had varying peak intensities across all the diatoms that were sampled. When analyzing tephra and sand grains included in the diatom bulk the aluminium content was generally the same or twice that of the oxygen peaks, fig 20 and 21. The two plots in graph 3.19 are representative of the high and low levels obtained for aluminium in diatoms. Raw and saturated diatoms returned the same representative results.

Observed surface deposits were of two definite types, those in the pores, images 3.19, 3.20, 3.21 and fig 3.19 made up the majority. The deposits on the diatom surface as in image 3.17 were also found but to a much lesser extent. In the EDS spectra of the deposits (fig 3.19) the deposits have a higher carbon content than the diatoms suggesting that these deposits are from coagulated colour material.

An effect that looks like surface mottling or dissolution was observed on the saturated diatoms. This effect was noticed on the thinner hymen surfaces, image 3.18, but was also observed on the edges of broken pieces of main diatom structures, image 3.22. If this is dissolution of the biogenic silica the increase in absorbance at high pH (i.e. above 5) may be due in part to dissolved silica and fragmented diatoms.

In image 3.20 the diatom surface appears mottled. This was only observed in the saturated diatoms. Image 3.19 and 3.20 were taken from the same slide and with the same scale settings. The difference between the two images suggests that the mottling effect is the result of silica re-deposition from solution.

The pH changes and silica dissolving into solution may be allowing localized reactions resulting in colour compounds forming deposits on the diatom surface, specifically in the pore structures. Pore size would allow for a higher hydraulic gradient in the pores compared to outside of the pore structure (Rushton, Ward et al. 1996; Cheryan 1998). Silanols have been shown to form compounds with organics via the hydrogen atom of the hydroxyl group, due to adsorption, that produces charge neutralization and enmeshment of a precipitate (Stumm 1992). Silanols are substantially stronger acids than similarly constructed hydroxyl derivatives of carbon (Voronkov, Mileshkevich et al. 1978).

The way the deposits appear within the pores is suggestive of a flow type deposit. Image 3.20 shows detail of this effect. The deposits are against the inner pore structure and around the pore rim as if part of a liquid flow deposition such as interception leading to impaction of the colloids, hydrodynamic interaction and electrostatic attraction may also be involved.

Chapter 4

Conclusions and implications

The stirred adsorption studies were undertaken to determine parameters for:

1- Upper and lower pH values for effective reduction of absorbance.
2- The efficiency of colour reduction as a function of the ratio of diatom additive to wastewater volume.
3- Mechanical factors necessary to give colour reduction at optimal dosage ratios and pH conditions.

This study has shown that pH has two effects:

1- Pulp and paper mill wastewaters undergoe a change in colour of the chromophores. The intensity increasing in a non-linear fashion with increasing pH, changing the wavelength of maximum colour, figure 4.1.

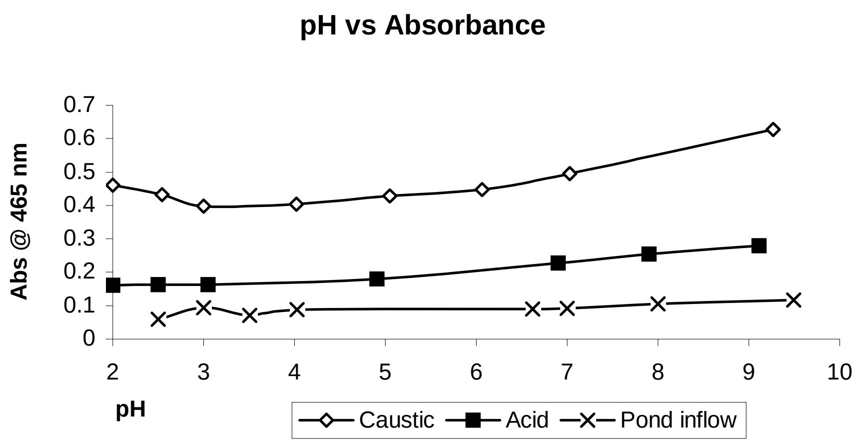


Figure 4.1: *Changes in absorbance with pH of wastewater. All tested absorbance data can be found in Appendix C.2.*

2- Changes in the chemistry of diatom surfaces with changing pH affect the efficiency of chromophore adsorption. The surface charge of biogenic silica and the adsorption potential for Al and Fe to biogenic silica is also pH dependant (Dixit and Van Cappellen 2002). The results of this thesis show that the most effective pH for colour removal was from 3.6 to 5.0.

The diatoms had a pH buffering effect when added to wastewaters. This effect was slower than the adsorption rate of colour material. After the addition of added wastewater aliquots, colour removal ceased until the pH was buffered to within the effective range. For the Tasman inflow waters in experiment 3, pH buffering was substantially reduced by the 38-hour point and absorbance reduction stopped, fig 4.2.

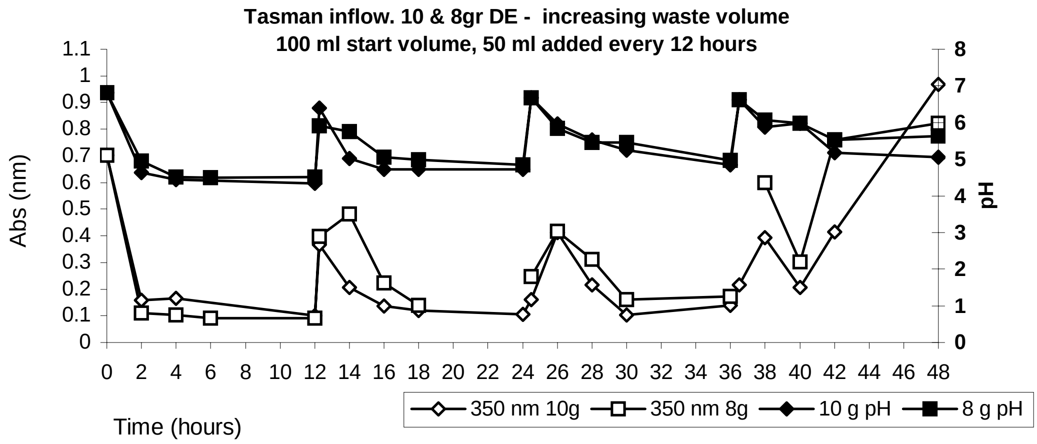


Figure 4.2: *The response of absorbance and pH to multiple doses of wastewater at 12-hour intervals. Experiment 3, for 8 & 10 g of diatoms*

6 g of diatoms to 100 ml of wastewater gave effective absorbance reduction for both acid and pond inflow waters, with minor affects due to low dosage of diatoms to wastewater. These effects were more obvious in the pond inflow results. In the case of continuously mixed diatoms with wastewater, best initial adsorption occurred with lower ratios of diatoms (8 g) to wastewater. As further

aliquots of wastewater were added best adsorption was achieved at higher ratios of diatoms (10 g).

As more wastewater was added the dose rate reduces, at 250 ml wastewater addition 6 g became 2.4 % (diatoms in weight to wastewater in volume) and the 10g became 4 %. For the acid stirring tests saturation was not achieved suggesting lower rates are achievable.

The requirements for specifying an ideal stirring time will vary depending on the end result. Within industry for example, compromises between efficiency cost and time are of importance (Hoyle 1999).

For acid wastewater, table 4.3, the initial absorbance was 0.142 (465 nm) with the minimum of 0.035 at 10 minutes of stirring, the reduction in absorbance achieved being 75 %.

The bulk of the reduction in absorbance occurred with in the first 30 seconds at a rate faster than the diatoms could be separated from the suspension, fig 4.3.

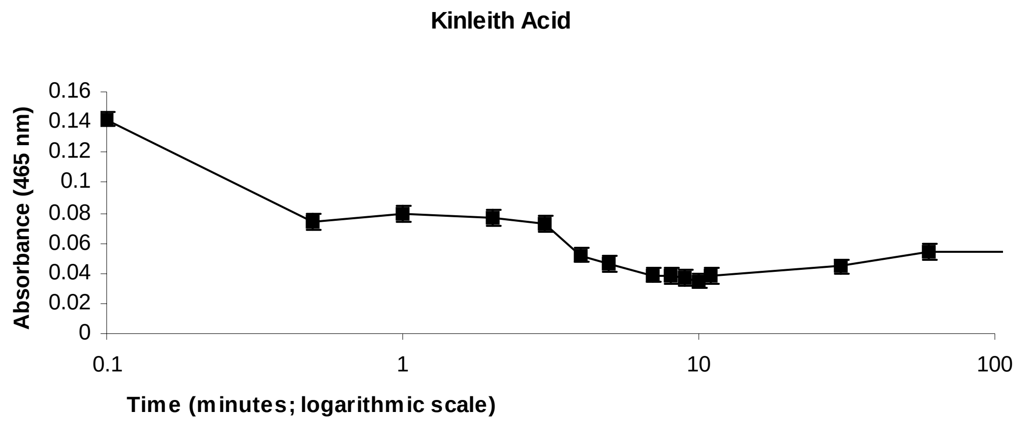


Figure 4.3: *Absorbance at 465 nm vs. Time for Kinleith acid wastewaters.. Error bars are +/- 0.005 nm for absorbance.*

Minutes	0.1	0.5	1	2	3	4	5	7	8
Abs (465nm)	0.142	0.074	0.079	0.077	0.073	0.052	0.046	0.039	0.038
Minutes	9	10	11	30	60	120	240	360	720
Abs (465nm)	0.037	0.035	0.038	0.045	0.054	0.054	0.051	0.052	0.039

Table 4.1: *Data points for figure 4.1.*

In order to design the most effective protocols for colour reduction by diatom dosage it is necessary to understand the nature of the interactions between the colour producing compounds and the diatoms. There are many forms of capture mechanisms that could be included when discussing methods of adsorption filter operation:

1) How do the colour materials get to the adsorption sites
2) How do the colour molecules react when they get to the adsorption site
3) How significant is diffusion within the diatoms of the colour molecules
4) How significant is fluid flow through the diatoms
5) What is the chemistry of the interactions between colour molecules and diatom surfaces, e.g. electrostatic, double layer repulsion and Van der Waals forces

Trying to assess the relative importance of the above listed mechanisms and their interactions in particle capture is difficult. Recognition of the various mechanisms is still important as a qualitative tool for the interpretation of experimental or practical results (Rushton, Ward et al. 1996). These forces are often grouped and reported as collection efficiency to particle size ratio, figure 4.1 (Yao, Habibian et al. 1971).

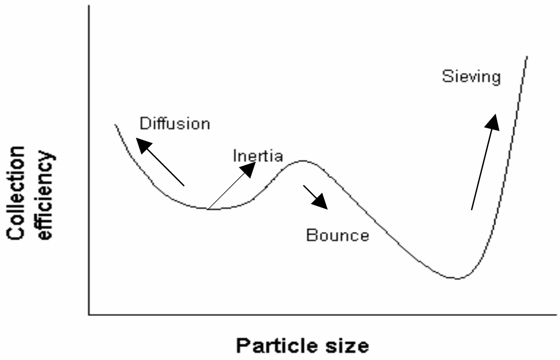


Figure 4.4: *Capture efficiency as a function of particle size, adapted from Yao, 1971.*

The fast 10-minute reaction time for absorbance reduction, the effective pH range and the biogenic silica structure and young age of the diatoms suggest silanol reactions with the wastewater colour material. Graphing ICP-MS results, fig 3.17 and 18, show that some cation exchange is occurring with increases of Al and Fe in solution. Thus coagulation affects from Al-OH and Fe-OH should not be discounted.

SEM images show the effects of diatom surface dissolution that would allow the release of silanols, Al-OH and Fe-OH into solution. Images of surface deposits of organic and siliceous nature show that the silanols and cations in solution have formed flocs with the colour material that is then adsorbed onto the diatoms.

Data in fig 4.3 show a two-stage effect with dissolution and then adsorption within 10 minutes stirring. The initial drop in absorbance over the first 3 minutes is due to coagulation by dissolved species. The second drop in absorbance from 3 to 10 minutes is due to the slower affects of adsorption by diatom floc interception and impaction.

Deposits are only observable in the diatoms that have been stirred at length this confirms the slower affects for deposit formation. The greater deposit formation in the diatom pores is explained as a result of hydrodynamic interactions and possible localized coagulation reactions in the pores.

The daily flow for Kinleith pulp and paper mill acid waste discharge averages 21.5 ML (Hejl 2006). At the rate of 10 % diatoms needed for 75 % reduction after 1 hour of mixing in absorbance the amount of diatoms per day can be calculated

21.5 Ml/day (21500 000 l day^{-1}) is equivalent to 21500 tonnes

= 896 tonnes / hour / day

@ 10 % diatoms = 89.6 tonnes of diatoms

10 g diatoms treated 3 volumes of acid wastewater. This is the equivalent to 89.6 tonnes of diatoms for 3 hours of wastewater flow or eight diatom doses a day of 716.8 tonnes/day. For a 6 % dose of diatoms the daily amount would be 430 tonnes.

Possible future study

True saturation of the diatoms had not been achieved, a method allowing for unlimited volumes of wastewater to be flowed without loss of the diatoms, but with the ability to keep pH within the optimum levels may achieve this.

Backwashing can also further the life of diatoms as a filter material, backwashing was not investigated fully in this study. More tests to ascertain ideal backwash liquids and pH operating ranges are recommended. Investigations into the backwashed liquor for potential uses as a product instead of another concentrated waste is a possibility. By using acid, caustic and neutral mill wastewaters to control pH and as backwash agents any design has greater potential as applicable technology to the pulp paper mill environment.

Studies into the mechanisms of adsorption by the diatoms used, in this respect known compounds with similar structure to the pulp mill wastewater compounds could be used to determine specific mechanisms and rates. The supernatant from stirring mixes could be separated from the diatoms before adsorption and applied to another adsorbent such as pumice, to test if surface deposits form as with the diatoms. More research in to the wastewater streams and the filtered deposits, as in the backwash material, may indicate paths of research.

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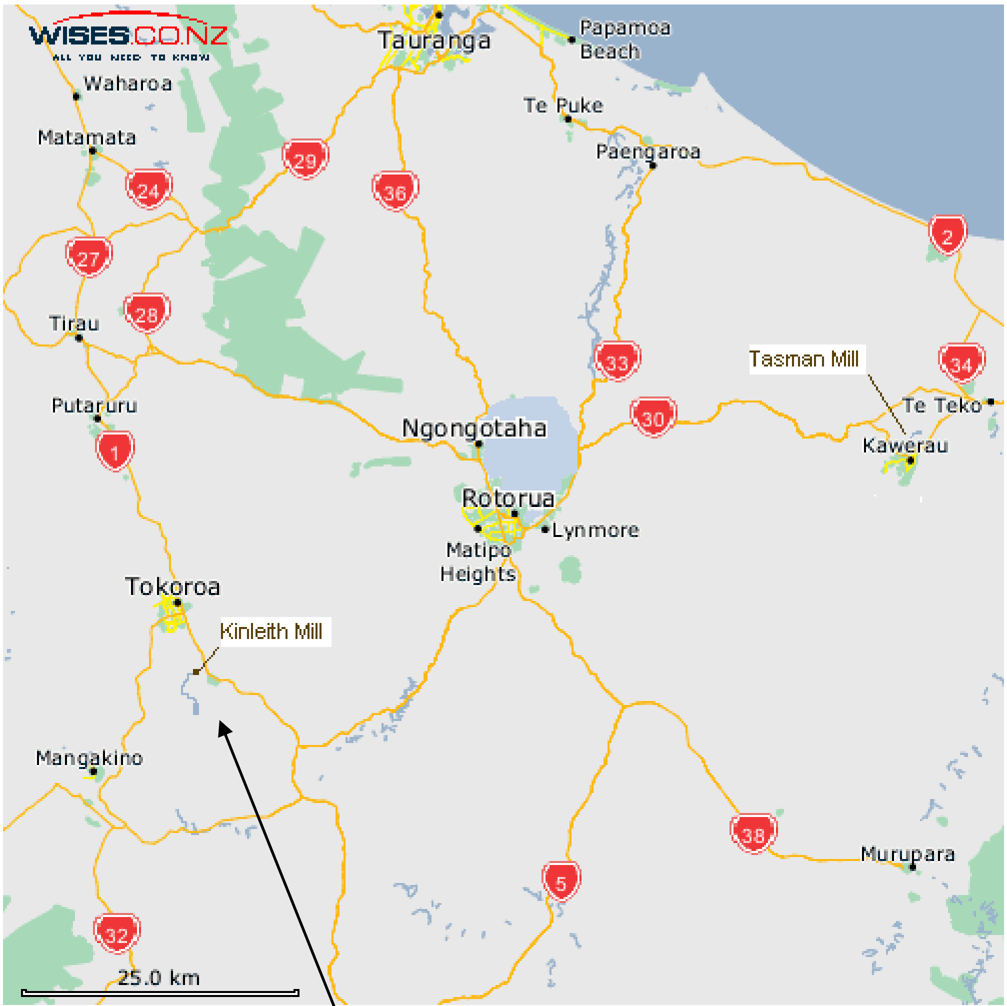
Appendix

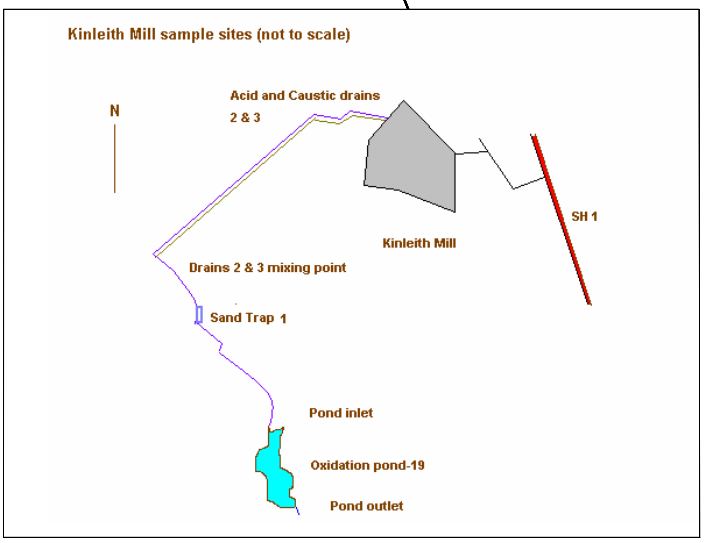
A. Maps

A-1. Rotorua Region



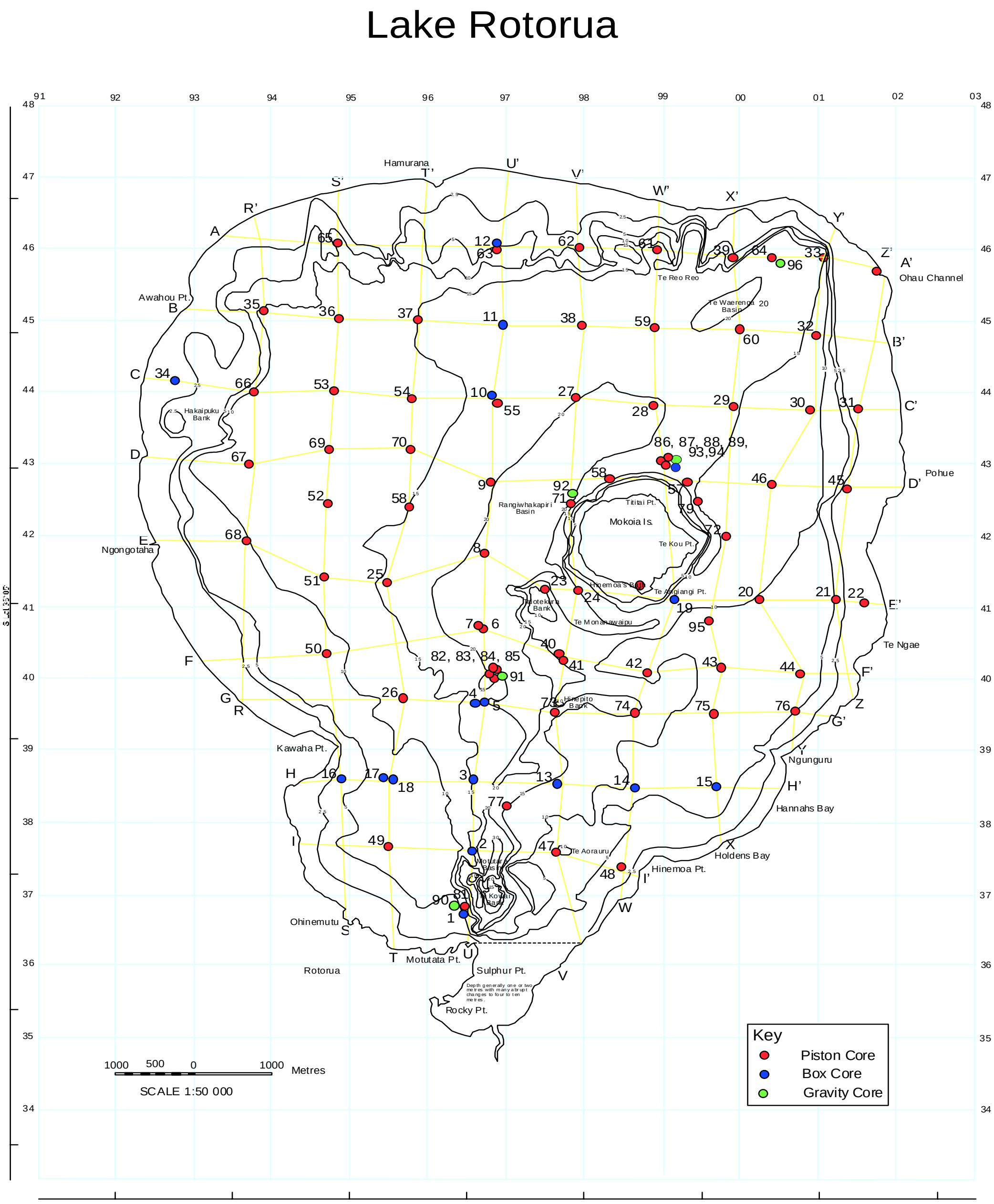
Map sourced from www.wises.co.nz 15-02-2007

A-2. Kinleith Mill sample sites



A-3. Diatom sample sites

The diatomaceous ooze samples were collected using a box corer from sites 3, 4, 10, 13, 14, 17 and 19.



(Hendy 2006; Pearson 2006)

B. Chloroplatinate Standard (SCION Rotorua)

ERG STANDARD OPERATING PROCEDURES

METHOD NUMBER: ERG-

METHOD: **Colour**

DATE: 14 November 2003

1. PURPOSE

The method described gives a blue for the colour of a wastewater based on a single spectrophototometric determination. It does not completely characterize the colour.

2. METHOD OUTLINE

Colour is determined by measuring the ratio of the absorbance of the unknown to that of a standard at a wavelength of 463nm (far blue). Solutions absorbing at this wavelength will appear yellowish. The chromophores derived from degraded lignocellulosic materials tend to absorb blue light, and determination is a convenient way to characterize their influence.

3. METHOD SOURCE

The method is based on NCASI Method. Refer to APHA-AWWA-WPCF Standard Method 2120. (18^{th} ed.) for more detailed information relating to colour.

4. SAFETY PROCEDURES

Depends on sample. No special precautions needed with reagents.

5. REAGENTS

See Standards.

6. GLASSWARE AND EQUIPMENT

UV/visible spectrophotometer set at 465 nm; cuvettes
Whatman GFC glass filters or equivalent
0.45 um cellulose acetate filter cartridges or vacuum filtration assembly
Small vial/beaker, minimum capacity 20ml

10ml pipette or syringe
1ml pipette
pH meter

7. STANDARDS

Chloroplatinate Colour Standard

Dissolve 1.246g pure potassium chloroplatinate (K_2PtCl_6) and 1.00g crystallized cobaltous chloride ($CoCl_2.6H_2O$) in distilled water with 100mL conc HCl and make up to 1000mL accuratedly.
See “Standard Methods” APHA-AWWA-WPCF for more information.

This solution has a Chloroplatinate colour of 500 mg Pt. L-1 (CPU, or Chloroplatinate units)

PH 7.6 NaOH/KH_2PO_4Buffer

Prepare by weighing out 6.85 g NaOH pellets, and 28.22 g $KH2PO_4.2H_2O$. Dissolve in 500 ml deionised water, cool and dilute to 1L

1% m/v NaOH solution in deionised water

1% m/v HCl solution in deionised water. Prepare bu adding 30ml concentrated (33%) HCl to 500ml deionised water, cool and dilute to 1 L

8. SAMPLE PREPARATION

Sample should have suspended and colloidal material removed by filtration through glass fibre filter paper. Turbid samples such as TMP based reactor effluent should be subsequently filtered through a 0.45um membrane.

The pH of the sample may influence the colour significantly.
Take 10ml of the filtered sample and add 1ml of pH 7.6 buffer. The buffer addition makes the pH adjustment easier.
Adjust pH to 7.5 $^{+}$- 0.05 by the addition of acid or alkali as necessary. Measure and specify the actual pH value.

Very highly coloured solutions will require quantitative dilution.

9. SAMPLE ANALYSIS

1) Adjust spectrophotometer to a wavelength of 465 nm. Zero the instrument using distilled water in 10mm glass or plastic cuvette.

2) Measure the absorbance of the unknown sample. If greater than about 0.3 the sample must be diluted quantitatively to within the range of about 0.05 to 0.3.

3) Measure the absorbance of the standard. It is normally about 0.13. The standard may be diluted to bring it closer in value to very lightly coloured samples.

10. CALCULATION

Colour sample (CPU) = Asample x 500 / Astd x 1.1

Reporting: Report the colour as Chloroplatinate Units (CPU) at 465nm at the measured pH. State whether the sample was filtered, and whether it was pH adjusted.

Appendix C

Absorbance and pH data

Appendix C contains the data that has not been presented in the main text. The data in Appendix C was used to produce graphs and tables in the main text.

1. Packed column filter:

Kawerau pond inflow

Total ml	420 nm	%Reduction	Elution T
Wastewater	0.410		
			12
250	0.036	91.22	12
350	0.207	49.51	12
450	0.232	43.41	12
550	0.237	42.20	12
650	0.23	43.90	12
750	0.224	45.37	12
850	0.224	45.37	12
950	0.211	48.54	12
1050	0.198	51.71	12
1150	0.192	53.17	15
1250	0.232	43.41	15
1350	0.22	46.34	15
1450	0.219	46.59	15

Tasman pond outflow (I)

Tasman outflow

Total ml	420 nm	%Reduction
Wastewater	0.360	
100	0.01	97.22
200	0.023	93.61
300	0.024	93.33
400	0.029	91.94
500	0.076	78.89
600	0.077	78.61
700	0.085	76.39
800	0.125	65.28
900	0.11	69.44
1000	0.111	69.17
1250	0.107	70.28
1500	0.11	69.44
1750	0.122	66.11
2000	0.118	67.22
2250	0.112	68.89
2500	0.114	68.33
2750	0.115	68.06

Tasman pond inflow (I)

Total ml	420 nm	%Reduction
Wastewater	0.317	
250	0.018	94.321767
500	0.042	86.750789
750	0.055	82.649842
1000	0.078	75.394322
1250	0.073	76.971609
1500	0.079	75.078864
1750	0.077	75.709779
2000	0.074	76.656151

Tasman pond in and outflow (Voronkov, Mileshkevich et al.) (not tabled in main body)

Tasman pond inflow

Volume ml	Elution T	300	340	440	480
Wastewater		0.993	0.685	0.276	0.192
250	21				
500	29	0.398	0.19	0.02	0.007
750	42	0.529	0.308	0.043	0.023
1000	32	0.544	0.339	0.037	0.025
1250	31	0.545	0.348	0.055	0.024
1500	34	0.556	0.349	0.048	0.048
1750	40	0.558	0.356	0.057	0.032
2000	47	0.568	0.394	0.072	0.025
2250	48	0.548	0.389	0.063	0.035
2600	45	0.494	0.284	0.05	0.033

Tasman pond outflow

Volume ml	Elution T	300	340	440	480
Wastewater		0.703	0.429	0.171	0.166
250	16	0.148	0.114	0.013	0.028
500	21	0.336	0.18	0.026	0.027
750	25	0.403	0.231	0.061	0.05
1000	31	0.403	0.236	0.059	0.032
1250	46	0.392	0.227	0.059	0.033
1500	54	0.389	0.203	0.043	0.028
1750	52	0.404	0.212	0.039	0.039
2000	54	0.403	0.228	0.041	0.036
2250	64	0.415	0.237	0.058	0.043
2600	70	0.62	0.334	0.068	0.034

2. Change in wastewater with change in pH (465 nm tabled in main body)

Kinleith Caustic

pH	9.27	7.03	6.06	5.05	4.02	3	2.54	2
480 nm	0.533	0.434	0.403	0.366	0.348	0.34	0.364	0.39
465 nm	0.627	0.495	0.447	0.429	0.403	0.398	0.432	0.46
400 nm	1.329	0.99	0.886	0.858	0.811	0.794	0.797	0.882
350 nm	>1.999	>1.999	1.864	1.85	1.743	1.71	1.624	1.761

350 nm readings took a long time to settle

1.999 readings were higher than the machines maximum scale

Kinleith Acid

pH	9.11	7.9	6.9	4.91	3.05	2.5	2
480 nm	0.254	0.226	0.201	0.15	0.145	0.142	0.143
465 nm	0.28	0.254	0.228	0.18	0.162	0.163	0.161
400 nm	0.575	0.52	0.478	0.404	0.36	0.355	0.355
350 nm	1.202	1.132	1.069	0.995	0.895	0.87	0.803

Tasman Pond inflow

pH	2.5	3	3.51	4.03	6.62	7	8	9.49
480 nm	0.053	0.084	0.058	0.08	0.08	0.087	0.093	0.108
465 nm	0.059	0.093	0.07	0.088	0.09	0.091	0.105	0.116
440 nm	0.072	0.114	0.083	0.102	0.103	0.108	0.128	0.13
400 nm	0.119	0.164	0.12	0.144	0.156	0.156	0.179	0.187
350 n	0.23	0.357	0.257	0.293	0.304	0.324	0.353	0.382

3. Experiment 1a: Single dose of diatoms

ClPt std nm	0.14			
Buffered pH	465 nm	CPU	DE (g)	
7.47	0.06	235.71	0.25	
7.57	0.042	165.00	0.502	
7.46	0.033	129.64	0.75	
7.48	0.049	192.50	1	
7.5	0.04	157.14	1.25	
7.53	0.031	121.79	1.5	
7.54	0.035	137.50	2	
7.51	0.043	168.93	3	
7.49	0.021	82.50	4	
7.48	0.021	82.50	5	
7.49	0.02	78.57	6	
7.54	0.02	78.57	8	
7.53	0.02	78.57	10	
7.55	0.061	798.81	0	Wastewater blank

4. Experiment 1b:

Single dose of diatoms

Name	Absorbance	Wastewater	2 hrs	4 hrs	6 hrs	12 hrs
T/inflow	350 nm		0.585	0.368	0.312	0.342
	400 nm	0.473	0.423	0.26	0.205	0.23
5 g	440 nm	0.394	0.356	0.206	0.167	0.182
	465 nm	0.363	0.331	0.186	0.143	0.16
	480 nm	0.351	0.319	0.169	0.145	0.15
	pH	6.81	5.3	5.26	5.24	5.09
	350 nm	0.701	0.318	0.196	0.34	0.17
T/inflow	400 nm	0.473	0.237	0.12	0.237	0.104
	440 nm	0.394	0.204	0.095	0.193	0.078
6 g	465 nm	0.363	0.18	0.076	0.17	0.064
	480 nm	0.351	0.173	0.077	0.163	0.058
	pH	6.81	5.24	4.94	4.85	4.74
	350 nm	0.701	0.11	0.103	0.09	0.09
T/inflow	400 nm	0.473	0.055	0.04	0.044	0.042
	440 nm	0.394	0.039	0.035	0.035	0.035
8 g	465 nm	0.363	0.036	0.03	0.03	0.03
	480 nm	0.351	0.031	0.03	0.03	0.03
	pH	6.81	4.95	4.52	4.49	4.52
Stir time (hours)			2	4		12
	350 nm	0.701	0.158	0.165		0.1
T/inflow	400 nm	0.473	0.116	0.098		0.053
	440 nm	0.394	0.093	0.084		0.04
10 g	465 nm	0.363	0.077	0.072		0.035
	480 nm	0.351	0.084	0.07		0.031
	pH	6.81	4.64	4.45		4.34

5. Experiment 2:

Double dose of diatoms

Double dose of diatoms							
	350 nm	0.17	0.106	0.113	0.164	0.115	
T/inflow	400 nm	0.104	0.058	0.08	0.09	0.07	
	440 nm	0.078	0.05	0.065	0.079	0.06	
6 + 2	465 nm	0.064	0.04	0.058	0.068	0.045	
	480 nm	0.058	0.038	0.065	0.068	0.043	
	pH	4.74	4.66	4.6	4.6	4.52	
Stir time (hours)		Wastewater	2	4	6	8	12
	350 nm	0.342	0.678	0.254	0.13	0.172	0.1
T/inflow	400 nm	0.23	0.467	0.185	0.085	0.113	0.068
	440 nm	0.182	0.391	0.164	0.069	0.1	0.042
5 + 5	465 nm	0.16	0.36	0.151	0.065	0.089	0.047
	480 nm	0.15	0.354	0.147	0.064	0.089	0.037
	pH	5.09	6.15	4.65	4.6	5.89	4.1

6. Experiment 3:

Pond inflow Multiple dose of wastewater

8 g diatoms - multi dose of wastewater
Time in hours from addition

Total stirring hours		Wastewater	2	4	6	12
	350 nm	0.701	0.11	0.103	0.09	0.09
T/inflow	400 nm	0.473	0.055	0.04	0.044	
	440 nm	0.394	0.039	0.035	0.035	
8 gr	465 nm	0.363	0.036	0.03	0.03	
	480 nm	0.351	0.031	0.03	0.03	
	pH	6.81	4.95	4.52	4.49	5.9
Stir time		Add 50ml-2	2	4	6	12
Total stirring hours		12.25	14	16	18	
	350 nm	0.398	0.482	0.223	0.139	
	400 nm	0.28	0.356	0.149	0.092	
	440 nm	0.24	0.295	0.122	0.073	
	465 nm	0.212	0.26	0.105	0.065	
	480 nm	0.197	0.242	0.1	0.059	
	pH	5.75	5.06	4.98	4.85	6.67
Stir time		Add 50ml-3	2	4	6	12
Total stirring hours		24.25	26	28	30	36
	350 nm	0.248	0.416	0.312	0.16	0.172
	400 nm	0.156	0.29	0.214	0.098	0.109
	440 nm	0.114	0.241	0.172	0.08	0.095
	465 nm	0.102	0.209	0.15	0.064	0.079
	480 nm	0.097	0.2	0.14	0.06	0.074
	pH	5.84	5.46	5.46	4.96	6.62
Stir time		Add 50ml-4	2	4	6	12
Total stirring hours		36.25	38	40	42	48
	350 nm		0.6	0.301	0.759	0.823
	400 nm		0.422	0.187	0.516	0.567
	440 nm		0.332	0.142	0.413	0.456
	465 nm		0.289	0.123	0.359	0.401
	480 nm		0.273	0.116	0.326	0.372
	pH	6.06	5.98	5.52	5.63	5.29

10 g diatoms - multi dose of wastewater
Time in hours from addition

Total stirring hours		0	2	4	6	12
	350 nm	0.701	0.158	0.165		0.1
T/inflow	400 nm	0.473	0.116	0.098		0.053
	440 nm	0.394	0.093	0.084		0.04
10 gr	465 nm	0.363	0.077	0.072		0.035
	480 nm	0.351	0.084	0.07		0.031
	pH	6.81	4.64	4.45		4.34
Stir time		Add 50ml-2	2	4	6	12
Total stirring hours		12.25	14	16	18	24
	350 nm	0.367	0.205	0.137	0.121	0.105
	400 nm	0.252	0.142	0.092	0.079	0.067

	440 nm	0.211	0.116	0.077	0.072	0.058
	465 nm	0.194	0.098	0.065	0.059	0.057
	480 nm	0.18	0.095	0.059	0.053	0.05
	pH	6.39	5.02	4.73	4.73	4.73
Stir time		Add 50ml-3	2	4	6	12
Total stirring hours		24.5	26	28	30	36
	350 nm	0.161	0.413	0.216	0.103	0.14
	400 nm	0.099	0.286	0.146	0.071	0.097
	440 nm	0.075	0.227	0.112	0.056	0.07
	465 nm	0.059	0.198	0.103	0.047	0.066
	480 nm	0.059	0.185	0.09	0.041	0.062
	pH	6.68	5.96	5.53	5.24	4.85
Stir time		Add 50ml-4	2	4	6	12
Total stirring hours		36.5	38	40	42	48
	350 nm	0.216	0.393	0.205	0.414	0.968
	400 nm	0.147	0.266	0.122	0.285	0.7
	440 nm	0.118	0.21	0.095	0.224	0.557
	465 nm	0.107	0.185	0.08	0.19	0.491
	480 nm	0.089	0.175	0.076	0.177	0.454
	pH	6.62	5.87	5.97	5.18	5.05

7. Experiment 5:

Acid multiple dose of wastewater

6 g diatoms - multi dose of wastewater

Time in hours from addition		0	2	4	6	12
Total stirring hours		100ml acid	2	4	6	12
Kinleith	350	0.69	0.575	0.505	0.449	0.408
Acid drain	400	0.284	0.209	0.225	0.182	0.15
	440	0.178	0.115	0.151	0.109	0.09
Kacid	465	0.142	0.091	0.123	0.084	0.059
6g -1	480	0.125	0.077	0.117	0.018	0.066
	pH	3.88	3.7	3.96	3.96	3.9
Total stirring hours		14		16	18	24
		Add 50 ml		4	6	12
	350	0.43		0.309	0.335	0.31
	400	0.171		0.113	0.124	0.13
	440	0.121		0.068	0.073	0.079
	465	0.106		0.057	0.07	0.075
	480	0.093		0.049	0.053	0.066
	pH	3.06		3.18	3.14	3.23
Total stirring hours		26			32	38
		Add 50 ml			6	12
	350	0.383			0.38	0.41
	400	0.145			0.153	0.184
	440	0.07			0.095	0.125
	465	0.065			0.082	0.111
	480	0.048			0.072	0.097
	pH	3.46			3.28	3.65
Total stirring hours		40		42	44	50
		Add 50ml		4	6	12

350	0.448		0.626	0.432	0.341
400	0.188		0.307	0.208	0.127
440	0.113		0.208	0.115	0.076
465	0.086		0.164	0.112	0.06
480	0.08		0.153	0.101	0.048
pH	3.58		3.68	3.72	3.76

10 g diatoms - multi dose of wastewater
Time in hours from addition

Total stirring hours		100ml acid				
Kinleith	350 nm	0.69	0.386	0.307	0.256	0.246
Acid drain	400 nm	0.284	0.134	0.113	0.099	0.088
	440 nm	0.178	0.078	0.059	0.067	0.049
Kacid	465 nm	0.142	0.052	0.051	0.052	0.039
10g -1	480 nm	0.125	0.047	0.045	0.042	0.026
	pH	3.88	3.62	3.9	3.89	3.81
Total stirring hours		14		16	18	24
		Add 50 ml		4	6	12
	350	0.344		0.267	0.295	0.299
	400	0.145		0.101	0.112	0.128
	440	0.095		0.053	0.065	0.072
	465	0.079		0.041	0.048	0.065
	480	0.077		0.043	0.043	0.061
	pH	2.94		3.02	3.05	3.14
Total stirring hours		26			32	38
		Add 50 ml			6	12
	350	0.281			0.29	0.284
	400	0.104			0.12	0.119
	440	0.063			0.079	0.079
	465	0.059			0.065	0.067
	480	0.03			0.05	0.062
	pH	3.3			3.15	3.54
Total stirring hours		40		42	44	50
		Add 50ml		4	6	12
	350	0.34		0.324	0.252	0.22
	400	0.142		0.146	0.103	0.086
	440	0.089		0.1	0.07	0.052
	465	0.076		0.079	0.058	0.047
	480	0.07		0.083	0.057	0.032
	pH	3.46		3.58	3.68	3.75

8. Rapid Response

Experiment 6:

Kacid	Wastewater	0.189	0.418	1.033	5.35
Kacid C.	Centrifuged	0.146	0.365	0.965	5.56
Kacid C.F.	Cntrfgd and filtered	0.1	0.283	0.784	5.5
stir minutes	0	0.1	0.238	0.784	5.5
5	5	0.039	0.112	0.34	4.13
10	10	0.043	0.107	0.34	4.06
20	20	0.073	0.154	0.398	3.95
30	30	0.055	0.135	0.38	3.92
40	40	0.044	0.124	0.336	4.06
50	50	0.046	0.125	0.37	3.95
60	60	0.054	0.124	0.384	4.02
70	70	0.08	0.149	0.407	3.93
80	80	0.035	0.094	0.336	4.07
90	90	0.037	0.111	0.345	4.06
100	100	0.047	0.114	0.35	4.11
110	110	0.045	0.118	0.358	4.05
120	120	0.054	0.117	0.354	4.07
		465 nm	**400 nm**	**350 nm**	**pH**
0	0	0.1	0.238	0.784	5.5
0.5	0.5	0.074	0.167	0.451	4.27
1	1	0.079	0.17	0.465	4.26
2	2	0.077	0.166	0.468	4.07
3	3	0.08	0.163	0.42	4.43
4	4	0.052	0.139	0.426	4.21
5	5	0.046	0.139	0.413	4.24
60	60	0.054	0.124	0.384	4.02
120	120	0.054	0.117	0.354	4.07

9. Wastewaters degradation during storage at 4^{o}C

	T-inflow stored at 4 C			
Date	5/30/2006	7/17/2006	7/21/2006	Average
Abs				
350	0.61	0.66	0.621	0.630
400	0.41	0.426	0.44	0.425
440	0.34	0.365	0.379	0.361
465	0.325	0.331	0.342	0.333
480	0.306	0.314	0.328	0.316
pH	6.18	7.08	7.12	6.79

K-acid stored at 4 C				
Date	4/3/2006	4/19/2006	7/17/2006	Average
465 nm	0.132	0.139	0.142	0.138
pH	3.42	2.01	3.88	3.10