SEMICONDUCTOR WASTEWATER TREATMENT WITH NATURAL STARCHES AS COAGULANTS USING RESPONSE SURFACE METHODOLOGY

by

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TABLE OF CONTENTS

CHAPTER THREE : METHODOLOGY 36

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATION

AAS	Atomic Absorption Spectrophotometry

ANOVA	Analysis of Variance
APHA	American Public Health Association
ASTM	American Standard Testing Methods
AWWA	American Water Works Association
BOD	Biochemical Oxygen Demand
CMP	Chemical Mechanical Polishing
COD	Chemical Oxygen Demand
DMSO	Dimetyl Sulfoxide
EDX	Energy Dispersive X-ray
NTU	Nephelometric Turbidity Unit
PACl	Poly Aluminium Chloride
R^2	Coefficient of Determination (Regression squared)
RSM	Response Surface Methodology
SBR	Sequencing Batch Reactor
SEM	Scanning Electron Microscope
SS	Suspended solids
TS	Total solids
TSS	Total suspended solids
X_1, X_2	Model terms

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1.2 Fatehah,M.O., Nik Norulaini,N.A., Teng,T.T. and Norli,I. (2005) Treatment of Semiconductor Wastewater by Natural Coagulants: Glutinous Rice, Tapioca and Potato Flour Using Response Surface Methodology. In: International Conference on Chemical and Bioprocess Engineering and the 19th Symposium of Malaysian Chemical Engineers, 8-10 December 2005, Promenade Hotel, Sabah, 631-637.

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RAWATAN AIR SISA SEMIKONDUKTOR DENGAN KANJI SEMULA JADI SEBAGAI AGEN PENGENTAL DENGAN MENGGUNAKAN METODOLOGI RESPON PERMUKAAN

ABSTRAK

Air sisa semikonduktor yang digunakan dalam kajian ini diambil dari sebuah syarikat semikonduktor antarabangsa di Pulau Pinang. Ciri-ciri influen semikonduktor bagi pH, keperluan oksigen kimia (COD), pepejal terampai (SS) dan jumlah pepejal (TS) adalah di antara julat 4-6, 70-1550 mg/L, 0.014-0.24 mg/L dan 8-188 mg/L masing-masing. Hasil analisis Energy Dispersive X-ray (EDX) untuk kajian, menunjukkan bahawa komposisi utama air sisa semikonduktor adalah silika. Kajian ini mempamerkan bahawa julat optimum pH bagi keterlarutan silika dalam air sisa sebagai pra-rawatan ialah pH 11-12, di mana sebahagian besar silika dapat disingkirkan selain daripada mengurangkan COD dan kekeruhan dalam tempoh semalaman. Bagi mempercepatkan proses rawatan, agen pengental asli seperti kanji ubi kayu, beras, beras pulut dan sagu dikaji sebagai pengganti agen pengental komersial i.e. aluminium sulfat (alum) dan polialuminium klorida (PACl). Satu perisian matematik, Metodologi Respon Permukaan (RSM), digunakan untuk membantu mengenalpasti keberkesanan dos dan masa tahanan untuk merawat air sisa. Kesan-kesan olahan pengentalan ke atas kekeruhan, COD dan SS dikaji dengan menggunakan persamaan kuadratik order kedua. Hasil perkiraan menunjukkan antara keempat-empat kanji yang digunakan, kanji beras pulut mempamerkan nilai-nilai R^2 yang tertinggi, 0.9860, 0.9320 dan 0.9560, bagi ketiga-tiga parameter iaitu kekeruhan, COD dan SS masing-masing. Ini diikuti oleh kanji sagu yang turut menunjukkan nilai-nilai R^2 yang tinggi, 0.9210, 0.9270 dan 0.8490, mengikut turutan parameter yang sama. Kanji sagu berjaya menurunkan kekeruhan yang paling tinggi tanpa mengira dos atau masa tahanan yang dikenakan. Untuk kanji beras, masa tahanan memberi kesan yang lebih dalam penurunan kekeruhan berbanding dengan dos, sementara bagi kanji beras pulut dan ubi kayu, kedua-dua faktor iaitu masa tahanan dan dos dan interaksi di antaranya banyak mempengaruhi hasil yang diperoleh. Dalam RSM, kesemua model yang digunakan untuk kanji asli dan terma-terma model adalah signifikan. Daripada model, nilai data sebenar dan data ramalan amat hampir persamaannya pada pelbagai koefisien regresi. Apabila menggunakan PACl sebagai agen pengental, nilai-nilai R^2 bagi kekeruhan, COD dan SS didapati adalah 0.6910, 0.6620 dan 0.8100. Bagi alum, nilai-nilai R^2 yang diperoleh adalah 0.6000, 0.8600 dan 0.3470 bagi parameter-parameter dalam turutan yang sama. Adalah terbukti dalam kajian ini, kanji sebagai polimer asli dan polielektrolit boleh digunakan sebagai agen pengental asli bagi rawatan air sisa semikonduktor yang mengandungi kepekatan silika yang banyak.

SEMICONDUCTOR WASTEWATER TREATMENT WITH NATURAL STARCHES AS COAGULANTS USING RESPONSE SURFACE METHODOLOGY

ABSTRACT

The semiconductor wastewater used in this study was obtained from a multinational semiconductor company located in Penang. The characteristics of the semiconductor influent for the pH, chemical oxygen demand (COD), suspended solids (SS) and total solids (TS) are in the range of 4-6, 700-1550 mg/L, 0.014-0.24 mg/L and 8-188 mg/L, respectively. The Energy Dispersive X-ray (EDX) results revealed that the major composition of the semiconductor wastewater is silica. The study indicated that the optimum pH range for silica solubility of the wastewater as pre-treatment was pH 11-12, which most of the silica was able to be removed besides lowering the COD and turbidity overnight. In order to expedite the treatment process, natural coagulants such as tapioca, rice, glutinous rice and sago starches were examined as a substitute for commercial coagulants i.e. aluminium sulfate (alum) and polyaluminium chloride (PACl). A mathematical software, Response Surface Methodology (RSM) was used as aid in determining the significance of the effect of dosage and retention time to treat the wastewater. The effects of coagulation treatment on turbidity, COD and SS were studied by employing a second order quadratic equation. Based on the equation, glutinous rice demonstrated the highest R^2 values of 0.9860, 0.9320 and 0.9560 for turbidity, COD and SS, respectively. The sago starch gave the second highest R^2 values of 0.9210, 0.9270 and 0.8490 in the similar according manner. Sago starch brought down the greatest level in the turbidity irrespective of the dosage or the retention time. When using rice starch, the retention time played a greater effect on the reduction of the turbidity with comparison to the dosage, while for glutinous rice and tapioca starches, both factors of dosage and retention time and their interactions shaped the outcome. The RSM showed that the models and the model terms used for the natural starches were significant. From the model, most of the actual and predicted values are closely agreed at various regression coefficients. When using PACl as a coagulant, the R^2 values obtained for turbidity, COD and SS were at 0.6910, 0.6620 and 0.8100 respectively. For alum, the R^2 values were at 0.600, 0.8600 and 0.3470 for the same parameters accordingly. It is proven in this study that starch as a natural polymer and polyelectrolyte can be used as a natural coagulant in the treatment of semiconductor wastewater that contains high concentrations of silica.

CHAPTER ONE

INTRODUCTION

1.1 SEMICONDUCTOR INDUSTRY

The electronic industry has been a fast growing sector of economy in many countries around the world for the past several decades. The industry is expected to continue its accelerated growth in the foreseeable future. Manufacturing in an electronic industry consists of a range of products of which semiconductor is an important one. The semiconductor is used in computers and their peripherals, communication, equipment, consumer electronic products, electronic control devices, scientific and medical test equipment. The semiconductor manufacturing involves a large number of complex and highly delicate processes including silicon growth, oxidation, doping, photolithography, etching, stripping, dicing, metallization, planarization, cleaning, etc. (Lin and Yang, 2004; Lai and Lin, 2004; Hollingsworth et al., 2005). There are over two hundred types of organic and inorganic compounds (proprietary and generic) involved in the manufacturing processes of semiconductor integrated circuits. Some of the steps in the sequence are wafer backgrinding, sawing, die attach, wire bonding, encapsulation, electroplating, trim and form, and marking (Wu et al., 2004; Hollingsworth et al., 2005).

1.2 CHARACTERISTICS OF SILICA AND SILICA WASTEWATER

Silica is one of the most abundant materials on the earth's surface; it has a formula of SiO_2 and it exists in both crystalline and amorphous forms. Quartz, tridymite, or critobalite are crystalline forms of silica and have a low solubility of about 6 ppm in water. Amorphous silica has a higher solubility of 100–140 ppm (Sheikholeslami and Bright, 2002). When silica in the form of monosilicic acid ($Si(OH)_4$) is dissolved in water, it will remain in the monomeric state as long as its concentration remains less than about 2 mM. However at higher concentrations monosilicic acid dimerizes and polymerizes to form (larger) polysilicic acids, the larger of which are of a colloidal size. Colloidal silica is also sometimes referred to as silica sol. Table 1 shows the size range definitions of particles in water.

Table 1 Size range of particles usually found in water samples (Sheikholeslami and Bright, 2000)

Type	Particle size (nm)	Stability
True solution	<1	Completely stable
Colloidal dispersion	1 – 500	Can remain dispersed for years
Suspension	>500	Settles rapidly

The presence of silica in water is due to the dissolution of silica based on the following reaction: $SiO_2 + 2H_2O \rightarrow Si(OH)_4$. Soluble silica in water is initially in monomeric state as monosilicic acid ($Si(OH)_4$) and is mostly un-ionized at natural pH levels. As pH increases, the degree of ionization increases; at a pH of 8.5 only 10% of the monosilicic acid is ionized and as the pH reaches 10, approximately, 50% is ionized.

Silica can be found in surface water and groundwater as particulates, colloids, polymers, or dissolved in the form of acids or hydroxides. Dissolved silica in water is normally measured as SiO_2 despite the fact that the exact form of dissolved silica is unknown. Average concentrations of silica in natural waters range between 0.1 and 0.55 mg/L. The solubility limit for silica in water is estimated at approximately 120 mg/L at 25^oC. The limited solubility of silica in water is the main reason behind the requirement of its removal in many water treatment and use practices (Freeman and Majerle, 1995).

1.3 TREATMENT OF SILICA WASTEWATER

Silica removal in field waters has been tested by many researchers using sodium aluminate, lime and soda ash (Ueda et al, 2003; Sheikholeslami et al., 2002). Sodium aluminate alone was unable to reduce the silica content significantly and it was observed that the silica concentration were still high even with high doses of sodium aluminate. The addition of soda ash to sodium aluminate only slightly improved the silica removal but further improvements were obtained when lime itself was added to sodium aluminate or both lime and soda ash were jointly added to sodium aluminate; this can be only due to increase in the pH of the solution. Silica polymerized faster at higher temperatures though silica solubility increases temperature. Increase in Ca, Mg and hardness in general increased the rate of polymerization (Ueda et al., 2003).

At neutral pH values, the presence of metals facilitates silica polymerization. However, at high pH values, in the presence of metals, silica precipitates as silicates get more viscous. As such, it is imperative to understand and identify the factors that affect silica polymerization and the methods for removing silica from water. In practice, silica removal is usually part of a lime-soda softening process where calcium, magnesium and alkalinity concentrations are reduced. In the lime softening process, silica will be reduced with the precipitation of magnesium hydroxide where silica is removed by adsorption on the magnesium precipitates. The precipitation and adsorption of silica by magnesium hydroxide are widely used in water treatment techniques for silica removal (Sheikholeslami et al., 2002).

Several treatment processes can be used for removal of silica from water. Such processes include: cold softening lime and soda ash, hot softening using lime and $Mg(OH)_2$ precipitate is formed in the process. Improved removal of silica in lime softening can be obtained by addition of coagulants such as ferric chloride, aluminium salts, and polymers. Again, the removal efficiency of silica depends on the amounts of iron and aluminium hydroxides formed. In situations where not enough precipitates of $Mg(OH)_2$ are formed during the softening process, addition of $Mg(OH)_2$ and/or $MgSO_4$ enabled the improvement of silica removal (Al-Rehaili, 2003).

Review of previous studies on silica removal using lime softening with and without coagulant aids showed that the removal efficiency is dependent on the solution composition. Important factors include pH, alkalinity, total dissolved solids (TDS), hardness, and silica concentration. Up to 90% removal of silica was obtained using hot lime-soda softening process of water containing 10 mg/L silica, 3.2 meq/L hardness, 2.7 meq/L alkalinity, and 275 mg/L TDS; while for the same water only 40% silica removal was reached using cold lime softening with ferric salts. Five processes, including coagulation-flocculation and several softening process alternatives were compared for evaluation of the effects of $Mg(OH)_2$ precipitates formed under alkaline conditions with reduction of silica from 18 to 5 mg/L. Lime softening with addition of sodium aluminates was able to reduce silica by 80% from an original concentration of 30–50 mg/L. Caustic soda as a single clarification chemical was found extremely competitive to the lime-soda ash process for silica removal. The addition of precipitation aids such as alum, sodium aluminate, or ferric chloride was found necessary for improved performance of the lime-soda ash process and reduction of silica to the acceptable level. Caustic soda as a single chemical was found very efficient for silica control in groundwater sources (Ndbigengesere et al., 1998).

Silica, both soluble and colloidal, can be removed from water to varying levels in neutral or slightly alkaline solution by co-precipitation with soluble metals which form insoluble hydroxides in situ, or by adsorption upon freshly formed insoluble hydroxides added to water. Although alumina should be the best adsorbent, magnesium hydroxide, however, is the most common reagent, requiring a relatively high pH, recirculation of sludge and a hot process. In laboratory studies, silica was adsorbed and precipitated by hydroxides of aluminium, iron, manganese and magnesium. With a 15 ppm $Al(OH)_3$ solution, the silica concentration dropped from an initial amount of 3 ppm to a residual value of 0.8 ppm; whereas with 30 ppm aluminium hydroxide, no measurable silica remained. Dissolved silica may also be adsorbed onto a surface such as ferric hydroxide, rather than precipitation as a discrete compound. Ferric hydroxide is precipitated from ferric sulfate by addition of sodium or calcium hydroxide for silica removal. In this case, a pH of 9.0 or greater is required. Silica is adsorbed onto the surface of insoluble magnesium compounds, such as $Mg(OH)_2$ or $MgCO_3$. If a natural water contains a considerable portion of magnesium hardness, then silica will be removed to a certain extent with concurrent precipitation with $Mg(OH)_2$. However, the chemistry of silica removal by magnesium hydroxide is unclear. Magnesium silicate (e.g. Mg_2SiO_2 (foresite)) may be formed, but the most likely mechanism is simple adsorption onto the surface of $Mg(OH)_2$. The Al^{3+} ion precipitates colloidal silica, but only in the pH range 4 to 5. It requires only one part Al^{3+} to precipitate 40 parts SiO_2. The Al^{3+} ion precipitates soluble silica in the pH range 5 – 11, but at least 4 parts Al are required for 1 part of SiO_2 (Reed et al., 1998).

Lime and magnesia (which can be made from magnesite) are commonly used for removing silica from water. They flocculate colloidal silica along with other precipitated or suspended matter and combine with and adsorb soluble silica. Silica is “hydrophilic”, however under some conditions where salts are present, it causes coagulation and become “hydrophobic”. Moreover, when organic flocculating agents are adsorbed onto the surface of silica, the surface definitely becomes hydrophobic. Coagulation has been considered to be the result of van der Waals attraction which draws two particles together at the moment of collision, unless opposed by a hydration barrier or by the electrostatic repulsion forces between the similarly charged particles, or both (Lai and Lin, 2003).

According to Ueda (2003), there are two factors that retard coagulation of silica; one being the “hydration” of the surface of the particles by a layer of water molecules hydrogen-bonded to the Si-OH groups and the second being the negative ionic charge on the particles at about pH 3.5 with the surrounding cloud of positive counter ions such as Na^+, forming the “double layer”. The mechanism of the coagulation of colloidal silica by electrolytes is still not well understood. It has been found that below pH 11, and above critical concentrations of salts of all the alkali metals, coagulation occurs because the particles become initially linked together by acid-base bonds, rather than Si-O-Si bonds. However, above pH 11, where the surface is covered by basic groups, sodium and lithium salts continue to bring about coagulation but potassium, rubidium, and cesium salts do not.

Sheikholeslami and Bright (2002) observed in their study that in a mixture of polyvalent metal salt and polysilicic acid or colloidal silica at low pH, co-precipitation occurred as the pH was raised to just below the pH at which the metal hydroxide was precipitated from the metal salt solution when no silica was present. Examples of such salts include Fe^{3+}, Cr^{3+}, and Ca^{2+}. Silica particles may also be coagulated by hydrolyzed aluminium ions. Flocculation of colloidal silica occurs with the addition of a polymeric or particulate colloid; the micelle or particle or which is adsorbed simultaneously on the surfaces of two silica particles, thus linking them together. Such adsorption occurs either because the agent is cationic and thus attracted to the negatively charged silica surface, or because it contains electron donor groups such as the oxygen of a polyether, and is held to the silica surface by hydrogen bonding. The latter only occurs at low pH.

The amount of flocculant added is critical, since a certain amount of flocculant is required to give complete flocculation, however if excess flocculant is added, the flocculant may act as a stabilizing agent. To prevent redispersion in the presence of excess flocculant, the colloid should first be coagulated

1.4 TREATMENT OF SEMICONDUCTOR WASTEWATER

The principals involved in treating semiconductor wastewater are almost the same as that for silica wastewater since more than 90% of the semiconductor wastewater is silica. According to Lien and Liu (2006), in Taiwan, coagulation- flocculation treatment by polyaluminium chloride and polymer mainly treats the wastewater in most of the semiconductor manufacturers. Control of the coagulant dosage is difficult since there is nanosize silica (SiO_2) in the wastewater. A large amount of ultra-pure water is extensively being used in rinsing the silicon wafer during fabrication since cleanliness of the silicon wafer is emphasized. Table 2 reveals the water quality of the semiconductor wastewater.

Table 2 Water quality of the semiconductor wastewater (Sheikholeslami et al., 2002)

Parameter	Semiconductor wastewater
pH	9.3 – 9.7
TS (mg/L)	4100 – 5300
SS (mg/L)	0 – 0.2
ABS (mg/L)	0.01 – 0.03
TP (mg/L)	1 – 2
Density (g/L)	~1
COD (mg/L)	175 – 500
BOD/COD	0.11 – 0.15
Color	Milky

Treatment of semiconductor wastewater has been taken up by several approaches. Lai and Lin (2003) used electrocoagulation of chemical mechanical polishing wastewater from semiconductor fabrication. Den and Huang (2005) also used electrocoagulation to remove silica nano-particles from the wastewater. Park et al. (2001) made a research on biological treatment of wastewater containing dimethyl sulphoxide from the semiconductor industry. Lin and Kiang (2003) carried out a combination treatment consisted of Fenton oxidation and sequencing batch reactor (SBR) treatments of high-strength semiconductor wastewater.

Hollingsworth et al. (2005) used an approach of anaerobic biodegradability and methanogenic toxicity of key constituents in copper chemical mechanical planarization effluents of the semiconductor industry. Semiconductor wastewater containing fluoride was treated by electrocoagulation-flotation to remove the fluoride (Hu et al., 2005). Series of chemical and physical treatments of chemical mechanical polishing wastewater from the semiconductor fabrication was adopted by Lin and Yang (2004).

A similar approach was also done by Sheikholeslami and Bright (2002) who used a pretreatment of coagulation and flocculation to remove silica and metals in order to prevent fouling of reverse osmosis membranes. Among the treatments mentioned, conventional coagulation might be inferior with comparison to the other treatments due to the extents of production sludge, longer retention time and added chemicals. One of the disadvantages of electrocoagulation is that it requires electricity as voltage which is a strong factor influencing the performances of electrocoagulation (Lai and Lin, 2004). Preliminary pH study has also been conducted on semiconductor wastewater (Badruk and Matsunaga, 2001; Sheikholeslami et al., 2002).

1.5 NATURAL COAGULANTS

Aluminium salts are the most common synthetic coagulants used in water and wastewater treatment all over the world. However, studies have shown that aluminium can cause harm to the environment (Reed et al., 1998; McCurdy, 2004). A cheaper yet effective natural coagulant was studied as a substitute for commercial coagulant to reduce the turbidity, chemical oxygen demand, and total suspended solids problems related to semiconductor wastewater. Natural coagulants of vegetables and mineral origin were used in water and wastewater treatments before the advent of synthetic chemicals. A study using *Moringa oleifera* as a coagulant by Ndabigengesere et al. (1995) showed that it was an effective natural coagulant which could be used in treating water just by using shelled or non shelled dry seeds. The action of *M.oleifera* as a coagulant is due to the presence of water soluble cationic proteins in the seeds. Moreover, the adsorption and neutralization of charges that occurred are the main mechanisms of coagulation.

Other natural coagulants have been used to treat water and wastewater. One such example was the use of cactus as a coagulant in water treatment by Zhang et al. (2006). Diaz et al., (1999) looked into the preliminary evaluation of turbidity removal by natural coagulants indigenous to Venezuela. *Catus latifera* and the seeds of *Prosopis juliflora*, were used to act as natural coagulants in a jar test measurement. Both materials produced comparable turbidity removals and were able to produce a final water whose turbidity was close to the required government standard.

1.6 PROBLEM STATEMENT

The demand for the cleanliness of the wafer is high, which leads to large amounts of ultra pure water being extensively used in rinsing of silicon wafers during fabrication. Management of semiconductor wastewater has become one of the major concerns due to the large quantities of water required and the treatment of the wastewater. Research and development in more cost effective technologies in water conservation and wastewater treatment are always a priority (Lien and Liu, 2006).

Effect of pH reduction or increase to extreme acidity or alkalinity respectively on semiconductor wastewater aiming at reducing COD, and its relation to turbidity is lacking. Hence in this study, pH adjustment of the semiconductor wastewater was pursued in order to determine its effectiveness as a pretreatment to reduce COD, turbidity and TSS.

The focus of previous researchers when using coagulation and flocculation techniques was to use synthetic polymer as the main coagulant. There had been concerns that synthetic chemical coagulant such as alum and ferric chloride are harmful as well as generating large volumes of sludge (Ndbigengesere et al., 1998) and the sludge produced will be categorized as scheduled wastes that require proper disposal according to the federal regulations under the Environmental Quality Act (Scheduled Waste Regulation, 2005). As such, an alternative solution is needed to determine the effectiveness in the use of natural coagulant to treat semiconductor wastewater. Natural coagulants have been tried in the treatment of lignin from wastewater (Ganjidoust et al., 1997), *Ipomoea dasysperma* on the decolorization of textile dye (Sanghi et al., 2006) as well as cactus as coagulant in turbid water treatment (Zhang et al., 2006). No natural coagulant has been used in treating the highly turbid semiconductor wastewater. Comparison in the effectiveness of natural coagulant as opposed to synthetic coagulant in treating semiconductor wastewater to reduce the COD, TSS and turbidity in complying to the requirements of the local regulation is thus appropriate.

Finally, this research covers the use of a systematic comparison of effectiveness of the various tested parameters which has not been carried out but whose use can facilitate determination of independent variables in optimizing the treatment.

1.7 OBJECTIVES

The objectives of this study are as follows:

- To study the effect of pH on the reduction of COD and turbidity of semiconductor wastewater.
- To determine the efficiency of different natural starches as coagulants in treating the COD, turbidity and TSS of semiconductor wastewater.
- To compare the efficiency of commercial coagulants, PACl and alum with the natural coagulants to remove the COD, turbidity and TSS.
- To analyze the significance of the coagulant concentrations and retention time on the COD, turbidity, and TSS using RSM.

CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

The electronic industry consists of manufacturing a wide range of products of which semiconductor is an important one. Semiconductor is used in computers, consumer electronic products, communication equipment, electronic control devices and scientific and medical test equipment. Semiconductor manufacturing involves a large number of complex and highly delicate processes which use a large quantity of water in various washing and cleaning steps. Among the various semiconductor manufacturing process, chemical mechanical polishing semiconductor represents an important operation (Lin and Kiang, 2003).

According to Lai and Lin (2004), there is a heavy reliance on the chemical mechanical polishing to reduce wafer topological imperfections and improve the depth of focus of lithography processes through better planarity. The increasing use of semiconductor slurry drives the demand for ultra pure water for slurry dilution, cleaning and rinsing wafers and equipment. This has led to a multifold increase in the volume of water consumed and subsequently the amount of wastewater generated.

The wastewater generated in the semiconductor manufacturing process may contain non-halogenated solvents, acids, bases, salts and other organic compounds. The effluent from the semiconductor process contains inorganic and organic contaminants that are derived from the slurry, the wafer, linearization and post polishing and cleaning processes. Contaminant solubility depends on several factors including pH and the oxidation-reduction potential of the solution. Direct discharge of the wastewater generated is strictly regulated due to the presence of various organics and/or inorganic compounds.

2.2 SEMICONDUCTOR WASTEWATER COMPOSITION

In a study carried out by Lin and Yang (2004), the semiconductor wastewater was milky in color apparently due to the presence of fine suspended oxide particles. The semiconductor wastewater also had high total solids (TS) contents of 4500 mg/L, but the suspended solids

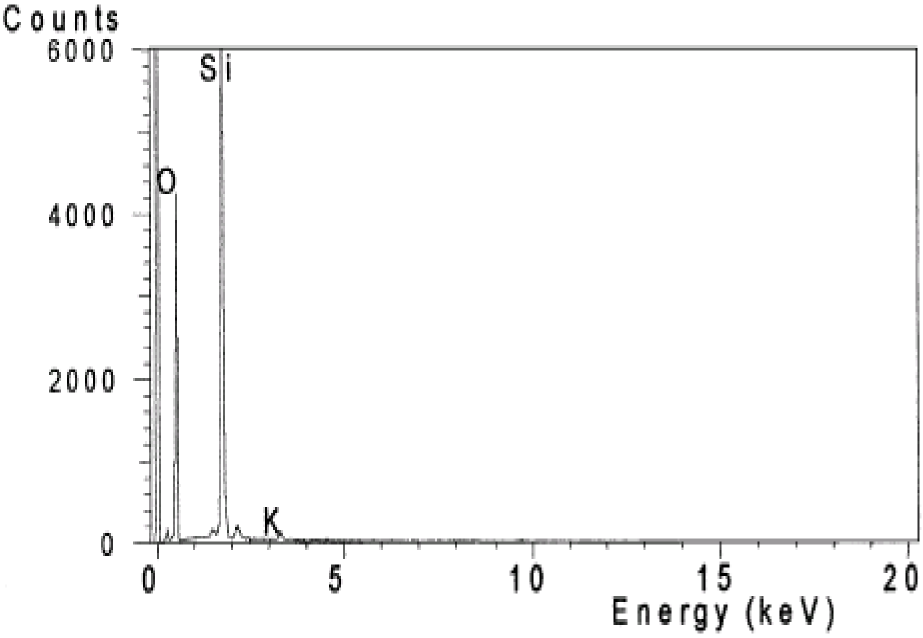
(SS) concentrations of both samples were negligible, being less than 0.2 mg/L. This was due to the fact that the size of the fine suspended oxide particles was less than the pore size 0.45 µm of the standard filter paper used for the SS measurements while the TS concentration was measured by drying the sample in a crucible which retained all the fine oxide particles.

Lin and Jiang (2003) found that the semiconductor wastewater used in their study had a pH 9.5 and very low suspended solids concentration at 10 mg/L, and high chemical oxygen demand (COD) concentration of over 70000 mg/L. They also found that the biodegradability of the wastewater as represented by the ratio of BOD/COD was low at 0.124, reflecting the existence of recalcitrant organic compounds. They further noted that the COD concentration of the semiconductor wastewater was due to mixing of the semiconductor wastewater with other processes wastewater streams that contained organic compounds, but little total solids. Hence, COD removal from the semiconductor wastewater is as important as the removal of fine suspended oxide particles if the semiconductor wastewater is to be upgraded to a level for general reuse purpose.

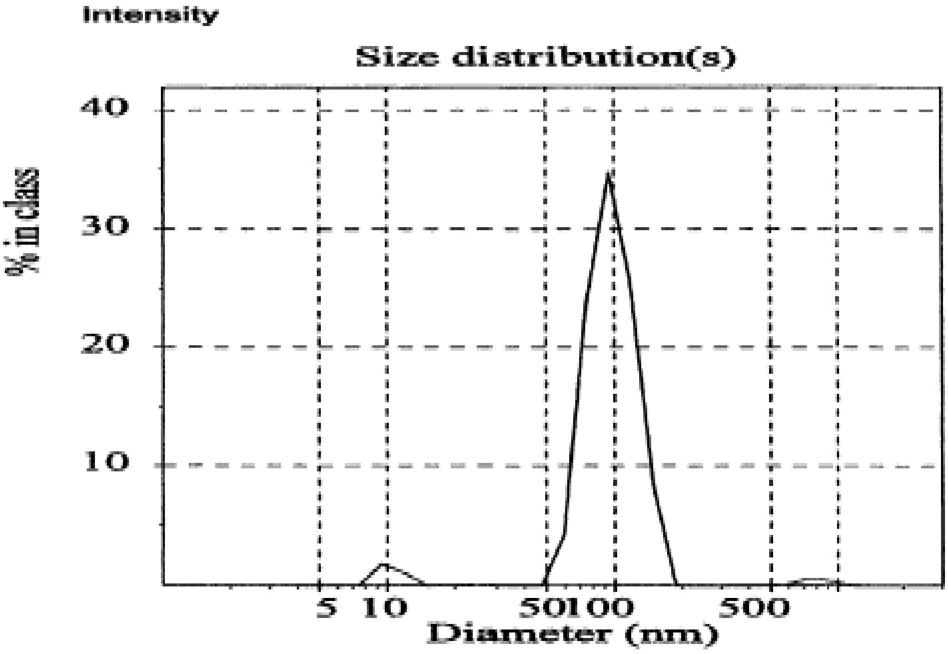
Fig. 1a displays the elemental composition determined by using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) method. From the composition, the fine oxide particles were identified as silicon dioxide (silica, SiO_2) which is the most popular type of oxides employed in the semiconductor slurry. Fig. 1b shows the size distribution of fine oxide particles in the semiconductor wastewater, as measured by a zeta potential meter. The oxide particles sizes fall within the narrow range between 50 and 200 nm with a great major of particle size around 100 nm which was more than 10 times smaller than the pore size of the filter paper for the SS measurement. This accounts for the very low SS and high TS.

In lower pH environment, silica can form aggregates or agglomerate. The aggregate and agglomerate were formed by chemical or physical attachment of silica particles. The SEM image of dry semiconductor wastewater sample with aggregated formation of silica particles is shown in Fig. 2.

The microscopic image clearly demonstrates the fibrous formation of the aggregate. The aggregate or agglomerate could also be formed in the original



(a) Elemental Composition



(b) Particle Size Distribution

Fig. 1 The EDX oxide particles in semiconductor wastewater (a) elemental composition and (b) their particle size distribution (Source: Browne et al., 2000) semiconductor slurry. They are not desirable and have to be removed by filtration before the semiconductor slurry is used (Lin and Yang, 2004). In wastewater, most inorganic materials appear in oxidized form. The majority of insoluble contaminants come from the slurry abrasive, which may include suspended particles of silica, alumina (Al_2O_3) and ceria (CeO_2) typically in a 50-500 ppm concentration after dilution. The particle size after the polishing process is 0.5 μm. Abrasion of the wafer surface also introduces other inorganic contaminants such as metals and metal oxides. Den and Huang (2005) assert that the soluble inorganic species that include oxidizers such as hydroxylamine and hydrogen peroxide must be reduced to a more innocuous form before being discharged.

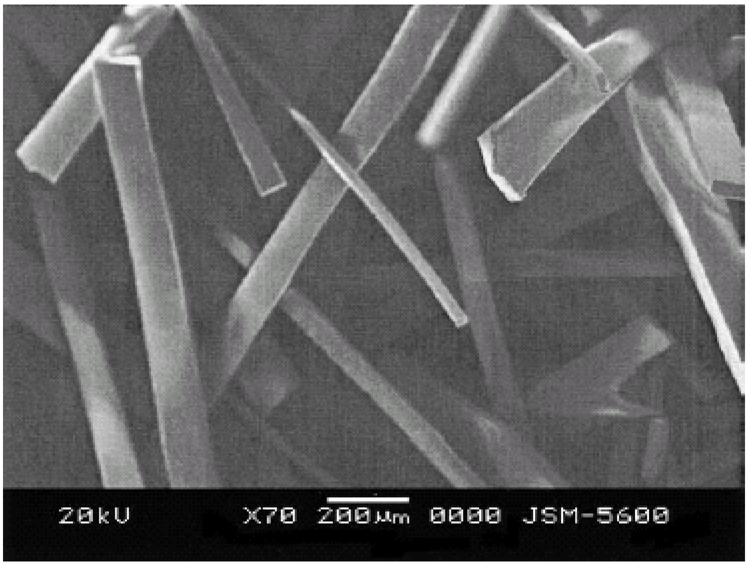


Fig. 2 The SEM image of silica agglomerates in the silica wastewater (Source Lin and Yang, 2004)

The organic materials found in the semiconductor effluents include metal complexing agents and surfactants whose solubility is usually pH dependent. Soluble copper complex and acid salt form at low pH but becomes insoluble at pH 5. The pH of the wastewater largely dictates the relationship of inorganic contaminants. In general, copper and other transition metals exist as insoluble oxides and hydroxides at elevated pH and under oxidized conditions. At low pH, copper and other transition metals are highly soluble. Silica and alumina display a maximum insolubility from pH 6 to 7. At pH >9, silica and alumina begin to dissolve and form soluble silicates and aluminium-hydroxo species.

2.3 SEMICONDUCTOR WASTEWATER TREATMENT

The typical water quality of the semiconductor wastewater has a pH range of 9.3 to 9.7, total solids of 4100-5300 mg/L and suspended solids ranging between 0-0.2 mg/L. The suspended solids (SS) concentrations are too small due to the oxide particle size to be measured by the standard filter paper used for SS measurement, which is 0.45 μm. The total solids (TS) concentration was measured by drying the sample in a crucible which retained all the fine oxide particles (Lin and Yang, 2004).

In addition, the wastewater has a high COD concentration, exceeding tens of thousands in units of mg/L, due to the mixing of the semiconductor wastewater with other process wastewater streams that contained organic compounds. Feeding this low biodegradable wastewater along with other wastewater streams to the activated sludge tanks places a considerable strain on the biological wastewater treatment system currently employed by the semiconductor manufacturer.

To overcome this difficulty and to improve the overall performance of the biological treatment process, separate treatment of this high strength semiconductor wastewater by alternative methods is needed. Removing the COD is as important as the removal of fine oxide suspended particles. The fine oxide particles have been identified as silicon dioxide (silica, SiO_2) and the oxide particle sizes fall within the range between 50 and 200 nanometer (nm) with a great major of particle size around 100 nm which was more than 10 times smaller than the pore size of the filter paper for the SS measurement.

Based in Fig. 2, the silica particles are geometrical and kept in suspension in the aqueous solution by pH adjustment. In a lower pH environment, silica can form aggregate or agglomerate. The aggregate and agglomerate were formed by chemical or physical attachment of silica particles (Hayashi et al., 1995).

Due to the complexity of the semiconductor wastewater, any single treatment method would be inadequate. Combination of physical, chemical and biological treatments could offer considerable synergistic advantages and be cost effective. There are a variety of treatment schemes available for the removal of suspended solids, and some organic materials in semiconductor wastewater.

a) Coagulation & flocculation

Coagulation and flocculation are effectively being used in chemical processes that involve neutralization of ion and particle surface charge. In the chemical coagulation process, the suspended particles are first aggregated by destabilization of the particle charge. The aggregated particles then form large, dense and rapid-settling flocs. The effects of matrix, molecular mass and ionic value of polymers on their interaction with suspended solids and dissolved organic matter were studied by Lurie and Rebhun (1997).

Significant differences were discovered in the interaction between low and high molecular mass polymers with particulates in the presence of soluble organics. Narkin and Rebhun (1997) examined flocculation processes in three types of waters containing suspended and dispersed solids and organic substances in the dissolved or colloidal form. The presence of anionic organic macromolecules and soluble organics in water increases the flocculant demand appreciable and affected water quality. Bidault et al. (1997) added fine but dense talc particles to an activated sludge aeration tank that improved floc formation and densified the newly created floc. The fine talc particles improved floc structure and formed stable and strong flocs.

Aluminium sulfate, ferrous and ferric chloride, and ferric sulfate are the conventional inorganic coagulants and their use demonstrates a single coagulation and flocculation action. Using PACl and synthetic polyelectrolyte as polymer, involves a two-step process of coagulation and flocculation. PACl can destabilize the suspended particles and promote aggregate formation and this step is called coagulation. However, the size of the aggregates might not be big enough to settle. As such another agent is used, typically polymer which can enhance large floc formation which eventually will settle. These separate coagulation and flocculation may explain the better performance when PACl was used with the polymer (Lin and Kiang, 2003). The amount of PACl and polymer and the initial wastewater pH have been reported to be important factors influencing the turbidity reduction efficiency of chemical coagulant (Ebeling et al., 2005).

Due to its high solid content, the semiconductor wastewater is distinctly different from most of the industrial wastewaters. Removal of the total solids thus has received the most attention. Browne et al. (1999) utilized ultra-filtration for removal of fine suspended oxide particles from the semiconductor wastewater. Belongia et al. (1999) studied the various facets of particle removal phenomenon by electro-decantation and electro-coagulation by using simulated alumina and silica precipitate. Golden et al. (2000) analyzed the effectiveness of chemical coagulation using a proprietary polymer coagulant followed by micro-filtration. The preceding researchers found that the combined process was effective in removing the fine suspended oxide particles and some heavy metals, if present. They suggested the mechanism to involve destabilization by coagulation. However, during the wafer surface cleaning process, the suspended oxide particle and chemical oxygen demand contents vary considerably over time.

Silica, both soluble and colloidal can be removed from water to varying levels in neutral or slightly alkaline solution by co-precipitation with soluble metals which form in-situ insoluble hydroxides, or by adsorption upon freshly formed insoluble hydroxides added to water. Magnesium hydroxide is the most common reagent, requiring a relatively high pH, recirculation of sludge and a hot process. In laboratory studies, silica is adsorbed and precipitated by hydroxides of aluminium, iron, manganese and magnesium. Magnesium silicate (e.g. Mg_2SiO_4 or foresite) may be formed, but the most likely mechanism is simple adsorption onto the surface of $Mg(OH)_2$. Dissolved silica may also be adsorbed onto a surface such as ferric hydroxide, rather than precipitation as a discrete compound as stated by Iler (1979). Ferric hydroxide is precipitated from ferric sulfate by addition of sodium or calcium hydroxide for silica removal. A pH greater than 9.0 is required. Al^{3+} ion precipitates colloidal silica, but only in the pH range 4 to 5. It requires only one part Al^{3+} to precipitate 40 parts SiO_2. The Al^{3+} ion precipitates soluble silica in the pH range 5 to 11, but at least 4 parts Al is required for 1 part SiO_2 (Sheikholeslami et al., 2002).

Silica is adsorbed onto the surface of insoluble magnesium compounds such as $Mg(OH)_2$ or $MgCO_3$. Lime and magnesia are commonly used for removing silica from water. They flocculate colloidal silica along with other precipitated or suspended matter and combine with adsorbed silica. Lime is often used as the first step in removing silica (Faust and Aly, 1993).

Polymeric or particulate colloid can flocculate colloidal silica by forming micelles or by the adsorption of particle simultaneously on the surfaces of two silica particles thus joining them together. Adsorption takes place based on the cationic characteristic of the polymer creating attention to the negatively charged silica surface. As low pH, adsorption can also take place due to the presence of electron donor groups such as oxygen of a polyether and held to the silica surface via hydrogen bonding. The amount of flocculant added is crucial since excessive addition of flocculant will actually stabilize the solution, while the correct amount will enhance flocculation. Also, in excess of flocculant, redispersion of silica particles can take place and to avoid this, the silica colloidal suspension must first be coagulated (Hasyahi et al., 1995).

Reed et al. (1998), studied the flocculation of colloidal silica with aluminium fractal polymers by aluminium magic angle spinning and silicon cross polarization magic angle spinning nuclear magnetic resonance as a function of aluminium concentration and pH. They ascribed the aluminium partitioning within silica flocs to a competition between structural rearrangement of individual aluminium polymers, which tend to adopt a flat conformation on the silica surface and excluded area effects originating from neighboring flocculant species.

Several commercially available polymers used as coagulant such as alum and ferric chloride are commonly used in wastewater and drinking water to remove suspended solids. However, recently alum and ferric chloride have been replaced by high molecular weight long chain polymers for flocculation of suspended solids. In a study by Ebeling et al. (2005), they found that some of the advantages of these polymers include lower dosage requirements, reduce sludge production, easier storage and mixing, no pH adjustment required and improve floc resistance to shear forces. Aside from that, the molecular weight and charge densities can be optimized to create designer flocculant aids and polymers bridge to many smaller particles.

Polymers or poly-electrolytes consist of simple monomers that are polymerized into high molecular weight substances (Metcalf and Eddy, 1991) and the molecular weights vary from 10^4 to 10^6 Daltons. Polymers can vary in molecular weight, structure (linear versus branched), amount of charge, charge type and composition. The intensity of the charge depends upon the degree of ionization of the functional groups, the degree of copolymerization and/or the amount of substituted groups in the polymer structure (Wakeman and Tarleton, 1999).

Organic polymers can be cationic, anionic or neutral. Polymers in solution have increased viscosities and low rates of diffusion which explains why mechanical dispersion into the water is needed. The mechanical mixing is accomplished by mixing vigorously to maximize dispersion, but caution must be taken so as not to exert excessive mixing so as to degrade the polymer or break the formed flocs (Wakeman and Tarleton, 1999). In using the high molecular weight long chain polymer in treating wastewater, the efficiency depends on the coagulation, flocculation and solids separation. These are then dependent on the polymer concentration, polymer charge (anionic, cationic or nonionic), polymer molecular weight and charge density and the raw wastewater characteristic. The waste characteristic includes particle size, concentration, temperature, hardness and pH. The physical parameters of the treatment, which include dosage, mixing energy, flocculation energy and duration are equally crucial as well as the discharge water treatment level required.

b) Electro-coagulation

Due to its high solid content, semiconductor wastewater is different from other industrial wastewater. Belongia et al. (1999) applied electro-decantation and electro-coagulation to study the various facets of particle removal. Fine oxide particles in semiconductor wastewater can be effectively removed by combining polymer coagulant and micro-filtration as reported by Golden et al. (2000). Electro-coagulation, which is an electrochemical treatment, is a low cost and efficient method for the treatment of water, wastewater and semiconductor wastewater (Lai and Lin, 2003). Further, it has been successfully used to treat potable water, aquaculture wastewater, textile wastewater, industrial wastewater and municipal sewage. The use of electro-coagulant to treat semiconductor wastewater is to remove fine oxide particles, improve the wastewater turbidity and lower the copper concentration in a single treatment. The size of the fine oxide particles falls within the range of 68 to 120 nm with an average particle size around 100 nm and remain as stable aggregates in the wastewater. After electro-coagulation, the fine oxide particles originally in stable suspension were destabilized, with average aggregate size estimated to be less than 20 μm and these aggregates have good settleablity and can be removed in less than 30 minutes.

Coagulation of suspended fine oxide particles is governed by different mechanisms such as double layer compression, surface charge neutralization, adsorption and interparticle bridging. The wastewater COD removal is caused by direct and indirect oxidation decomposition or organic pollutants in the electro-coagulation process. The electro-coagulation or electrochemical process is known to have two major oxidations on the wastewater: direct and indirect oxidations (Lin and Chang, 2000). Direct oxidation occurs on the anodic surface and is due to surface adsorption and decomposition of pollutants. Indirect oxidation occurs in the bulk liquid phase and is caused by the strong oxidants and is highly dependent on the wastewater conductivity.

By combining chemical pretreatment, micro-filtration and ion exchange, James et al. (2000) were able to remove the oxide particles and copper from copper semiconductor wastewater. Kruilik et al. (2001) found that the treatment process using proprietary polymer coagulant and micro-filtration was also effective in removing copper ion from copper semiconductor wastewater. Previous work as mentioned has shown successful removal of fine oxide particles and copper ions from the wastewater. However, the majority of the semiconductor wastewater from semiconductor fabrication contains more than just two pollutants. As mentioned earlier, semiconductor wastewater effluents contain significant amounts of organic compounds as reflected by the high COD. Without simultaneously removing the dissolved organic compounds, treatment of the semiconductor wastewater would be inadequate. The succeeding steps involved the removal of COD as well as the color. The fine oxide particles in the semiconductor wastewater are generally 68 to 120 nm with an average size of 100 nm. These sizes are smaller than the pore of the filter paper used to determine suspended solids and can easily pass through the pores. The oxide particles and aggregates are removed by filtration or redispensed by sonification. However, electro coagulation can destabilize the originally stable suspension of particles of the wastewater. The size of the aggregates can range from 49 to 141 µm with an average size of 17 µm. These aggregated particles can easily settle completely in half an hour. The coagulation of suspended oxide particles is governed by different mechanism, which includes double layer compression, surface charge neutralization, adsorption and interparticle bridging.

c) Fenton oxidation

Some semiconductor wastewater is complex and the complexity demands for multiple treatment method. Physical, biological and chemical methods can be combined in dealing with such wastewater. The combination of physical, chemical and biological treatments could offer a considerable synergistic advantage and be cost effective.

Lin and Jiang (2003) studied the treatment of a high strength semiconductor wastewater which was characterized by a strong dark color, high chemical oxygen demand concentration, presence of refractory volatile organic compounds and low biodegradability. They adopted the combined approach of using physical, chemical and biological methods consisting of air stripping, modified Fenton oxidation and sequencing batch reactor (SBR) method, respectively. Their treatment sequences were able to lower the COD concentration from as high as 80000 mg/L to below 100 mg/L and completely eliminate the wastewater color. The treatment process starts with air stripping using a packed column, operated at 70^{o}C for 180 minutes that removed over 95% of the isopropyl alcohol from the wastewater (initial IPA concentration was 35 000 mg/L). Isopropyl alcohol is an important solvent used for cleanings in the semiconductor manufacturing process and present in significant quantity in the wastewater. The wastewater effluent after the air stripping undergone Fenton oxidation after some dilution and the COD was removed more than 95%. The final step uses SBR treatment to further remove the COD up to 100 mg/L limit.

Fenton oxidation is capable of decomposing the recalcitrant organic chemicals in the wastewater, leading to considerable enhancement of the wastewater biodegradability. Chemical oxidation using Fenton reagents have been found to be effective in treating various types of industrial wastewater.

The treatment efficiency of Fenton oxidation is high pH dependent in order to remove COD and turbidity. Lin and Jiang (2003) discovered that treatments have been shown to be very effective between pH 2-5. The dosage of Fenton reagents, such as $FeSO_4$, is an important operating factor in Fenton oxidation. A high concentration of $FeSO_4$ will reduce the efficiency of COD removal; however the actual value will depend on the different types of organic contents present. The same goes to the feeding rate of the oxidizing agent used, H_2O_2 which also has an influence on the removal of COD in the semiconductor wastewater. The effect of temperature is also influential in affecting the outcome of the oxidation. Higher temperature accelerates generation of hydroxyl radicals and thus oxidation reaction. However in many cases, air stripping and Fenton oxidation are still inadequate to bring down the COD. The two former techniques need to be followed by sequencing batch reactor. They obtained COD removal of more than 86% at 12 hour cycle, compared to only 76% at 6 hour cycle. They concluded that as long as operating parameters are properly maintained, good performance of the SBR treatment can be expected.

2.4 NATURAL COAGULANTS

As expounded in the preceding section, coagulant plays an important part in areas of wastewater treatment. However, some types of inorganic coagulant that are widely being used have several disadvantages such as large dosage requirement, less effective, harmful to human body with the synthetic organic coagulant being expensive and toxic. Aluminium salts are the most common synthetic coagulants used in water and wastewater treatment all over the world. However, studies conducted by Mallevialle et al. (1984) raised doubts about the advisability of introducing aluminium into the environment. In fact studies done by AWWA (1990), indicated that there are several serious drawbacks of using aluminium salts such as Alzheimer’s disease and similar health related problems associated with residual aluminium treated waters.

Ferric salts and synthetic polymers have been used as alternatives but with limited success due to the fact that their impact on living beings is also not fully known (Ndabigengesere et al., 1995). Due to the high cost of synthetic polymers such as PACl and other chemicals for conventional water treatment, exacerbated with secondary pollution problem, alternative coagulants are preferable and can be found locally, thus offering an economical viable choice as well as non polluting (Sanghi et al., 2002). According to Jahn (1988), natural coagulants extracted from plants and animals are workable alternatives to synthetic polyelectrolyte as they are biodegradable, safe to human health and have a wider dosage range for flocculation of various colloidal suspensions, as well as cost effective. Natural coagulants have been used to treat drinking water for many centuries. For example, the Nirmali tree produced seeds that were used to clarify turbidity in surface water over 4000 years ago (Schultz and Okun, 1983) and according to Jahn and Hamid (1979), the Sudanese women discovered clarifying properties in the seeds of *Moringa oleifera* trees. Other natural extracts that have been reported to have similar traits include tamarind (*Tamarindius indica*), guar plant (*Cyamopsis psoraloides*), red sorella (*Hibiscus sabdariffa*), fenugreek (*Trigonella foeman*) and lentils (*Lens esculenta*).

These plant sources can all perform as effective coagulant aids at high water turbidities and can reduce the required alum doses by as much as fifty percent. There also has been a tremendous increase in the use of guar gum (*Cyamopsis tetragonolobus*) in wastewater treatment and *Cassia tora* and *Cassia angustifolia* have also been studied as coagulant aids by Sanghi et al. (2002). These natural coagulants posses several advantages compared to alum. The sludge volume is lower for the natural coagulant and the natural alkalinity is not affected by the treatment process.

Natural macromolecular coagulants have bright future and are concerned by many researchers because of their abundant source, low price, innocuity, multifunction and biodegradable. Much research have been done on the natural coagulants such as cactus (*Cactaceous opuntia*) by Zhang et al. (2006), *Moringa oleifera* (Ndabigengesere et al., 1995), and Ipomoea dasysperma seed gum by Singh et al. (2002). The origin of the cactus is mainly from the torrid and subtropics and the plant had received greater attention due to its nutritious and medicinal components such as proteins, amylose, malic acid, resin, vitamin and cellulose. Studies done indicated that cactus has similar properties as those seeds of *M. oleifera*, hence it too has potential as coagulant.

Zhang et al. (2006) studied the coagulation performance of cactus to act as natural macromolecular coagulant and discovered high turbidity removal efficiency. *Cactus latifera* and the seeds of *Prosopsi juliflora* were studied by Diaz et al. (1999) to act as natural coagulants using synthetic water with added kaolin to create turbidity. These two plants are indigenous to Venezuela and have similar properties to those described for natural coagulants. Using jar tests measurements, both materials produced comparable turbidity removals from average 150 NTU to 5 NTU. The findings are comparable with those obtained for *Moringa oleifera* extracts and compared to aluminium sulfate dose, the two plant sources required lower doses.

Moringa is a tropical plant belonging to the family *Moringaceae* and early studies have shown that the plant is non toxic and being recommended to be used as a coagulant in developing countries (Jahn, 1988). Encouraged by the results of the studies, many developing countries have used this plant as a viable coagulant in water and wastewater treatment (Sutherland et al., 1989). Water soluble extracts of *Moringa oleifera* seeds have been studied as a natural coagulant and the active ingredient have been suggested to be cationic peptides (Gassen et al., 1990). Numerous other laboratory studies have so far shown that *M.oleifera* seeds possess effective coagulation properties (Muyibi and Evison, 1995) and are not toxic to humans or animals. They are quite efficient in reducing turbidity and microorganisms from raw waters.

Other natural coagulants that are not from plant source include chitosan studied by Ganjidoust et al. (1997) and Meyssami and Kasaeian (2005). Chitosan is a natural cationic polyelectrolyte that is suitable to act as coagulant for the treatment of industrial and wastewater because they are safe and has no environmental impacts. It has been used to treat oil wastewater (Meyssami and Kasaeian, 2005) and pulp and paper wastewater (Ganjidoust et al., 1997).

In recapitulation, natural coagulants of vegetable and mineral origin have been used before the advent of chemical salts, but they have not been widely used because of the lack of scientific understanding of their mechanism and effectiveness. Recently however, current research is oriented toward the possible use of other types of coagulant, involving different types of flour, typically used in domestic cooking such as sago, tapioca and potato starch. These are all natural macromolecules and their use in treating silica semiconductor wastewater compared to alum and polyacrylamide chloride (PACl) is tested in this research.

2.5 RESPONSE SURFACE METHODOLOGY (RSM)

Response surface methodology (RSM) is an optimization approach commonly used in industrial process control and engineering where the goal is to find levels of input variables that optimize a particular response (Dhungana et al., 2006). The responses and the corresponding factor are modeled and optimized using the RSM. RSM is a technique consisting of (a) designing of experiments to provide adequate and reliable measurements of the response, (b) developing a mathematical model having the best fit to the data obtained from the experimental design and (c) determining the optimal value of the independent variables that produces maximum or minimum value of the response.

Response surface methodology (RSM) is a collection of statistical and mathematical technique useful for developing, improving and optimizing process (Lee et al., 2006). Basically, this optimization process involves three major steps: performing the statistically designed experiments, estimating the coefficients in a mathematical model and predicting the response and checking the adequacy of the model (Bandaru et al., 2006). It is a designed regression analysis meant to predict the value of a dependent variable based on the controlled values of the independent variables and for seeking the optimum conditions for a multivariable system efficiently.