CHARACTERIZATION AND TRANSFORMATION OF HYDROFLUORIDE NANO-SIZED PARTICLES IN SEMICONDUCTOR AND CALCIUM CHLORIDE: INFLUENCE IN pH

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ABSTRACT

Semiconductor wastewater contains high organic and inorganic compounds generated from several highly complex and delicate processes. The wastewater is generally divided into three different main streams, i.e. fluoride containing, acid base and chemical polishing. In this research, a preliminary study was conducted on the characterization and the transformation behaviour of hydrofluoride (HF) nano-sized particles in semiconductor wastewater within a pH range of 2 to12. The initial pH of HF wastewater suspensions was recorded at 6.35. At each adjusted pH, the surface charge and particle size were measured using the dynamic light scattering technique. It was found that HF nano-sized particles were negatively charged from pH 7.51 to pH 10.9 while between pH 2 to 7.49 and pH 9 to 12, they were positively charged. The pH of point of zero charge was found at pH 7.5 with a particle size of 4880 d.nm. Between pH 9 to pH 12, partial disaggregation was observed with a reduced particle size of about 83.54%. Further analysis was conducted on calcium chloride ($CaCl_2$), a coagulant that is used to treat HF in semiconductor wastewater. Surface charge and particle size were measured at each pH value within the same pH range. The initial pH value of CaCl2 was recorded at pH 5.75. Experimental data indicated that $CaCl_2$ is generally negatively charge with an average particle size of 767.9d.nm. The objective of the findings in this study is the fundamental key information that will later ascertain the optimization wastewater treatment processes that will be conducted. Implementation of these zeta potential and particle size measurements by using the pH_{PZC} of the wastewater as a point of reference will help determination of optimum dosage range via interaction (aggregation and disaggregation process).

Keywords: Particle size, pH, semiconductor wastewater, surface charge, hydrofluoride.

INTRODUCTION

A semiconductor is a substance commonly a solid chemical element or composite that can be used to conduct electricity under some specific conditions but not others. Semiconductor being used in many electrical circuits because it can control the flow of electrons making it a good medium for the control of electrical current. Its conductance varies depending on the current or voltage applied to a control electrode, or on the intensity of irradiation by infrared (IR), visible light, ultraviolet (UV), or X rays.

Therefore, semiconductor become an important electronic industry in Malaysia. It is extensively used in mobile devices (smart phones, tablets), storage devices (cloud computing, data centre's), optoelectronics (photonics, fibre optics, LEDs), embedded technology (integrated circuits, PCBs, LEDs) medical test equipment and electronic control devices [1]. Due to increasing demand, average annual growth of semiconductor industry increases rapidly and is expected to continue in the foreseeable future[2]. Study have shown that the electrical and electronics (E&E) industry is the leading sector in Malaysia's manufacturing sector, contributing significantly to the country's exports (33.4%) and employment (23.7%) [3]. The global semiconductor market was expected to grow at a compound annual growth rate of about 15 per cent from 2015 to 2019 and it been strengthen by the development of the industry through its Economic Transformation Programmed which is expected to create an incremental gross national income (GNI) impact of RM53.4 billion and create 157,000 new jobs by 2020 [4].

This industry involves several highly complex and delicate processes that consist of over a several steps of silicon growth, oxidation, doping, photolithography, etching, stripping, dicing, metallization, planarization, cleaning and etc[5]. Semiconductor manufacturing is also become one of the largest water-consuming industries since a huge amount of water is required during the cleaning and rinsing process of semiconductor wafers production[6, 7]. Wastewaters are produce by manufacturing processes including photolithography, photo resist stripping, etching, pure water washing and so on [5, 8, 9]. A large quantity of hydrofluoric acid is currently used in the industry unit such as photovoltaic cell manufacturing and electronics plants[10]in order to perform the manufacturing process activities. The concentration of fluoride in semiconductor wastewater is exceed 1000 mg/L and at a low pH which correspond to a huge treat to the environment [11]. Other than that, different organic and inorganic compounds including organic solvents, ammonium hydroxide, and phosphoric acid, are utilized during the manufacturing processes [12].

Semiconductor wastewater generated from fabrication facility is normally separated into three main streams: fluoride containing, acid base and chemical polishing. These separation practiced is due to pollution prevention and waste minimization purposes. The wastewater generated from semiconductor industry generally contains high levels of total ammonia nitrogen (TAN), fluoride (F-)[10] and phosphate (PO4-P). Research shows that, many contamination of heavy metal or metalloid has enter the water system from semiconductor manufacturing activity [13-15]. The existing of the significant nutrient substances will induced water eutrophication which excessive richness of nutrients in a lake or other body of water that causes a dense growth of plant life and death of animal life from lack of oxygen. As they exist in large quantities in the water bodies, large amounts of algae and microorganisms would breed, resulting in a higher dissolved oxygen depletion and fish toxicity[16, 17].

Reported in Taiwan, around 350–700m3 day^{-1} of fluoride-containing wastewater, with fluoride concentrations from 500 to 2000mg L-1 is generated by the rinsing and cleaning operations in a typical 8-in semiconductor fabrication facility [18]. This contaminant may trigger some of environmental issues especially fluoride and the concentration is more than 1000 mg/L [10, 18]. Treatment of fluoride-containing wastewater efficiently has been important for environmental engineers in Taiwan due to the fast development of the semiconductor industry. In Malaysia, fluoride containing wastewater may be a major concerned. Acceptable conditions for discharge of industrial effluent or mixed effluent as Regulation-11 (Environmental Quality (Industrial Effluent) Regulations, 2009) in Environmental Quality Act 1974, stipulates permissible limits for effluent discharges from industrial and services premises is 2 mg/L for Standards A and 5 mg/L for Standard B. In general, Standard A is applied if the point of discharge into the river is upstream from a water intake point for consumption or water catchment areas. Instead of that, Standard B is applied if the point of discharge into the river is downstream from a water intake point for consumption or water catchment areas. Even though fluoride is one of the necessary elements of the human body, the excessive fluoride intake can result in bone disease (pain and tenderness of the bones) and children may get mottled teeth [19]. Continuing drinking of water holding high fluoride content can lead to the problem of softening bones, ossification of tendons and ligaments and several neurological damages in other cases[20, 21]. These type of wastewater will cause groundwater contamination when enters to the surface water. According toWorld Health Organization(WHO), the safe prescribed fluoride level in drinking water, is less than 1.5 mg/L.

Many techniques have been studied and practice to answer the problem of HF wastewater including chemical coagulation with calcium salts [22-24]; precipitation using polyaluminum chlorides; adsorption onto montmorillonite [25, 26] or calcite[27]; electrocoagulation [28-30]; precipitate flotation[21]; and reverse osmosis [31, 32]. The cheaper way to remove fluoride from industrial wastewaters is by using chemical precipitation[33]. One of the studies is to investigate the simultaneous removal of fluoride (F-) from semiconductor wastewater by chemical precipitation using magnesium salts and which fluoride present could significantly inhibit the struvite crystallization [16]. Suspended matter and fluoride are simultaneously eliminated by combining coagulation and electro-flotation [10]. Study was also done on removal of fluoride and turbidity from semiconductor industry wastewater by combined coagulation with electro flotation and adsorption using activated clay [25].

Calcium chloride ($CaCl_2$) will be the main focus as coagulant to remove fluoride for this research. The purpose of selecting calcium chloride ($CaCl_2$) is because these coagulant were normally practice in the industry. Calcium chloride ($CaCl_2$) have a functions as a coagulant or precipitant, often together with flocculation. Coagulation consist of charge neutralization in which a cationic species (Ca++) combines irreversibly with a negatively charged pollutant. Precipitation generates an unsolvable substantial that resolves out, e.g., $CaCl_2$ reacts with fluoride to form insoluble calcium fluoride (CaF). Flocculation agglomerates small charge-neutralized, coagulated and precipitated particles to enhance settling and filtration.

This coagulant is often used together with a flocculants. In reducing fluoride ions from wastewater generated by the aluminium, steel, metal finishing, electroplating, glass, ceramic, phosphate rock, fertilizer, TV tube, and fluoride chemical sectors, calcium chloride being used because it provides calcium ions and pH adjustment. Add on lime to make known to calcium ions and adjust pH have been practice by many industries. The highly soluble $CaCl_2$ provides more calcium ions than lime without increasing pH. Use of $CaCl_2$can lower dewatering and scavenging costs while decreasing sludge as much as 50%.

MATERIAL AND METHODOLOGY

Experimental materials

A semiconductor wastewater was obtained from the fabrication company located at Kulim Hi-Tech. The untreated semiconductor wastewater is divided into two pits, fluoride-containing wastewater (known as HF wastewater) and chemical mechanical polishing wastewater (CMP wastewater). Only HF semiconductor wastewater being collected since the scope of this study is to focusing on their characterization and behaviour. The untreated HF semiconductor wastewater was collected and keep in the 20L polyvinyl chloride (PVC) bottle with sealed caps. Currently, the fabrication company is generating a huge volume of wastewater. The existing treatment consists of conventional method coagulation-flocculation process using $CaCl_2$, Poly-Aluminium Chloride (PAC) and polymer.

A 35% of Calcium Chloride ($CaCl_2$) was used as the stock solution throughout the experiments. The concentration of the stock solution was prepared to dilution of $CaCl_2$ 100 mg/L concentration was prepared as follow:

Equation 2.1 was used to prepare the stock solution

$$M_1V_1 = M_2V_2 \quad (1)$$

Where;
M_1 = Initial sample concentration (mg/L)
V_1 = Initial sample volume (L)
M_2 = Sample concentration required (mg/L)
V_2 = Sample volume required (L)

The pH of the solution sample and coagulant was adjusted by adding either dilute hydrochloric acid (HCl) or sodium hydroxide (NaOH). The stock HCl and NaOH solution of 0.25M was freshly prepared by dissolving a reagent grade HCl and NaOH in deionized water. The effect of pH on surface charge and size of particles was studied. The pH turned into adjusted via including a certain quantity of HCl (0.25M) or NaOH (0.25M) to 100 ml of studied sample beneath mixing with a magnetic stirrer (300 rotations per minute). The pH of the studied sample became measured before and after addition of acid or alkali. For each range of pH adjustment a brand new part of pattern changed into taken, i.e. to each 100 ml of sample the acid or base was delivered best one time. When pH was adjusted the pattern became taken with the aid of a syringe and switch to the cell or polystyrene cuvette. Make sure all the procedure need to do wisely and to make sure there is no air bubble in the cell and the cell need to wipe with a tissue paper to prevent any dust on the cell surface. Fail to follow the procedure may affect the accurately of the reading.

Experimental procedures

In the characterization study of HF semiconductor wastewater and $CaCl_2$, the magnetic stirrer was turned on and set at 300 rpm continuously. During each test run, 100ml of HF semiconductor wastewater or $CaCl_2$ 100 mg/L concentration was place in the sample container. A stable temperature of 25˚C was maintained for all test runs. The stirrer velocity have been discovered to be adequate to provide decent mixing in the electrolytic cell, and yet was not strong enough to break up the flocs formed during the treatment methodology. The raw HF semiconductor wastewater have been use without dilution in the sample cell while $CaCl_2$ is being dilute to 100 mg/L concentration. The initial pH, surface charge and particle size have been record before the pH was adjusted to the pH range of 2 to 12. The pH of the sample was continuously monitored using a digital pH meter.

The surface charge for HF semiconductor wastewater as well as $CaCl_2$ was determined according to the Smoluchowski equation while the particle size was measured using the dynamic light scattering (DLS) method with the Zetasizer Nano ZS (Malvern Instruments, UK). Small particles in suspension undergo random thermal motion known as Brownian motion. This random motion is modeled by the Stokes-Einstein equation. Below the equation is given in the form most often used for particle size analysis,

$$D_h = \frac{k_B T}{3\pi \eta D_t} \quad \text{(Stokes-Einstein equation)} \qquad (2)$$

The calculations are handled by instrument software. However, the equation does serve as important reminder about a few points. The first is that sample temperature is important, at it appears directly in the equation. Temperature is even more important due to the viscosity term since viscosity is a stiff function of temperature. Finally, and most importantly, it reminds the analyst that the particle size determined by dynamic light scattering is the hydrodynamic size. Each sample were measured for two times and to determine the surface charge and particle size. Ten sub-runs to determine the surface charge with a delay of 5 s between them. The purpose of the delay time is to stabilized and ease the system. While five sub-runs with 5 s delay for determination of particle size.

RESULTS AND DISCUSSION

Characterization for HF semiconductor wastewater

The concentration of H+ and OH- are measured by pH. At pH values below the point of zero charge (PZC), particle charge can be more positive or negative depending on the presence of those ions. The characteristic of raw HF semiconductor wastewater have been compared to the Standard A and B of Environmental Quality (Sewerage and Industrial Effluent) Regulation 2009 under the Environmental Quality Act 1974 and the Fifth Schedule Paragraph 11(1)1a) Acceptable Condition For Discharge of Industrial Effluent or Mixed Effluent for Standard A and B. From the Table 1. , pH for raw HF semiconductor wastewater collected is allowable since the value is in the borderline of the standard given.

Table 1. Characteristics of raw HF semiconductor wastewater and Standard A and B of Environment Quality (Sewerage and Industrial Effluent) Regulation 2009 and Fifth Scheduled.

Parameters	Raw HF semiconductor wastewater	Standard A	Standard B
pH	6.35	6.0 – 9.0	5.5-9.0
Fluoride, F^- (mg/L)	35.58	2.0	5.0
Particle size (d.nm)	872.6	N/A	N/A
Surface charge (mV)	+13.65	N/A	N/A

However, the contents of fluoride were classified higher since the concentration for raw HF semiconductor wastewater is 35.58 mg/L exceed the concentration allowable in Standard A and B. This high concentration of fluoride could be contributed by the cleaning and rinsing process in semiconductor fabrication activity.

Characterization of HF semiconductor wastewater study on surface charge and particle size as a function of pH.

In order to gain a better understanding of the pH effect on HF semiconductor wastewater surface charge and aggregation, the sample was titrated with HCl acid and NaOH over the pH spectrum of pH 2 to pH 12.the pH value with almost neutral charge is called the isoelectric point. The trends of surface charge and particle size for particle by varying the pH value from pH 2 to pH 12 are study and presented in Figure.1 and Figure. 2. The initial pH of the HF semiconductor wastewater determined at pH 6.35 with the average surface charge +13.65 and average particle size of 872.6 d.nm. As the pH was increased (Figure. 1) the surface charge is found stabilize at +6.68 with a standard deviation of ± 1.09 (+6.68±1.09 mV) and suddenly increased up to the maximum at pH 6.5 were the surface charge were 19.2 and start to decline gradually and reach the point of zero charge (pH_{pzc}) was measured at pH 7.5. By increasing the further pH, the surface charge become positively at pH 11 and pH 12.

The particle particle size of HF semiconductor wastewater is plotted as a function of pH in Figure. 2. The particle particle sizes are found to slightly increase in average at 4578 d.nm(±709.88d.nm) in range of pH 7.5 to 8.5. Above pH 7.5, particle sizes is rapidly increase to a maximum value at the PZC with value greater than 4880 d.nm indicating strong aggregation when the particle charge is neutralized. The size were increased from pH 6.35 to 7.5 with the value recorded at 872.6 d.nm and 4880 d.nm.

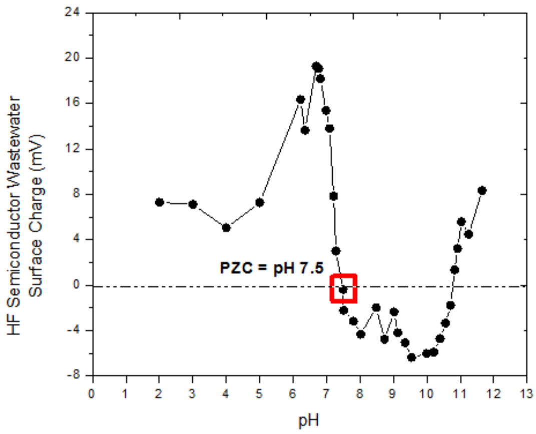

Figure 1. HF semiconductor wastewater surface charge variation as a function of pH. The initial pH determined at pH 6.35 with the average surface charge +13.65 and average particle particle size of 872.6 d.nm.

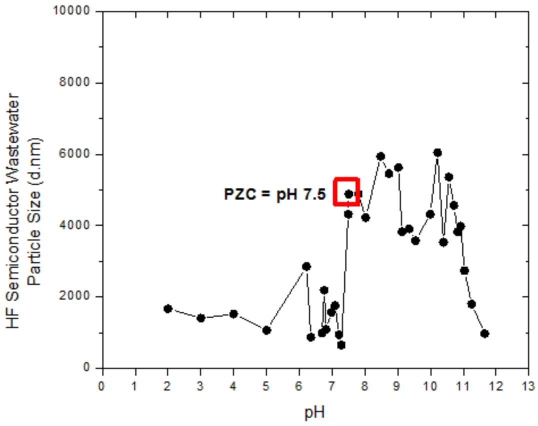

Figure 2. HF semiconductor wastewater particle size as a function of pH. The particle size at pH 7.5 which corresponding to particle zero charge (PZC) is around 4880 d.nm.

Characterization of Calcium Chloride ($CaCl_{2)}$ study on surface charge and particle size as a function of pH.
Calcium chloride 100 mg/L concentration was prepared by diluting a commercially available solution of 35% concentration with deionized water. This solution was obtain from the semiconductor fabrication company. The titration curve of CaCl2 100 mg/L were determined by adjusting pH from 2-12 with HCl or NaOH at variable concentration. The initial pH determined at pH 5.75 with the average surface charge -8.20 and average particle particle size of 767.9 d.nm.CaCl2 consider exhibit negative surface charge and constant particle size in the pH domain 2-10. As shown in Figure. 3, the value of surface charge for CaCl2 is fluctuated with the average size about 534.96 d.nmand standard deviation of ±190.39 (534.96±190.39). Then at the highest pH value the particle is rapidly increase due to alkali dissolve in $CaCl_2$ form a calcium hydroxide and sodium chloride.

$2\ NaOH_{(aq)} + CaCl_{2(aq)} = Ca(OH)_2 + 2\ NaCl$ 3.1

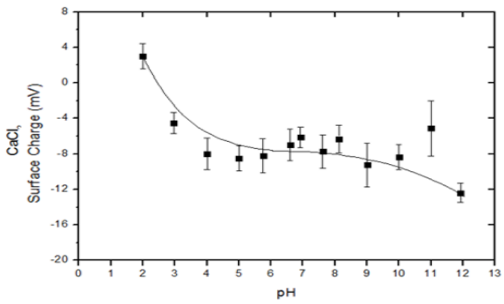

Figure 3. Calcium Chloride (CaCl2) surface charge variation as a function of pH. The initial pH determined at pH 5.75 with the average surface charge -8.20 and average particle particle size of 767.9d.nm.

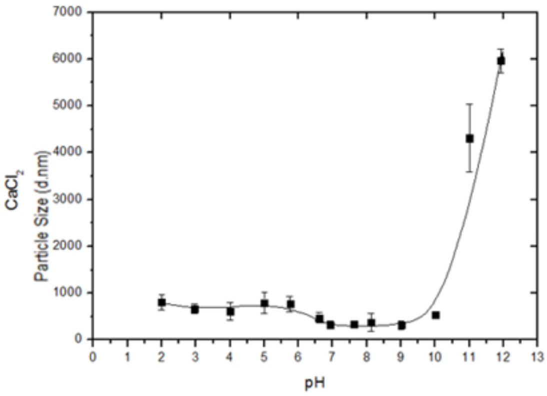

Figure 4. Calcium Chloride (CaCl2) particle size as a function of pH.

CONCLUSION

In this study, the characterization and behaviour of HF semiconductor wastewater and $CaCl_2$ were studied. Surface charge and particle size measurement were applied in order to obtain the point zero charge (pH_{pzc}) for the pollutant research. There are many different way in treating fluoride in semiconductor wastewater but in these method it help to understanding into the reason of aggregation and disaggregation behaviour which important in wastewater treatment design. From the Figure.1 aggregation were identified at range of pH 7 to 8.5. As a conclusion, the finding clearly define the interaction between HF semiconductor wastewater and $CaCl_2$can be done. Recommended to perform the interaction at pH 7.5(pH_{pzc}) consider constant pH of CaCl2 100 mg/L concentration.

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