HEAVY METAL IONS REMOVAL BY LIGNOCELLULOSICS MATERIALS DERIVED FROM LEAVES OF NIPAH AND OIL PALMS

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ABSTRACT

Heavy metal ions such as lead, copper and nickel are toxic elements which have a relatively high toxicity at low concentration. Lignocellulosics materials such as nipah leaflet, nipah leaf stalk, oil palm leaflet and oil palm leaf stalk had been studied as adsorbents for the adsorption of these heavy metal ions from aqueous solutions. Activated carbon had been used as reference for comparison under the same conditions. Different leaf samples showed considerable variations in their adsorption capacity for the adsorption of Pb^{2+}, Cu^{2+} and Ni^{2+} ions. Activated carbon had the highest adsorption for Pb^{2+} (29.11 mg/g) and Ni^{2+} (7.56 mg/g) whereas oil palm leaflet was observed to posses the highest adsorption capacity for Cu^{2+} ions (9.80 mg/g). The adsorption capacities of various leaf samples were observed to be affected by the particle size of adsorbents, pH of the metal solutions, initial concentrations of the metal solutions and mixed heavy metal ions solutions. Continuous column experiment was shown to be very effective in removing heavy metals. Almost all (>99%) of the heavy metal ions had been removed from aqueous solutions using this experimental approach. Lignocellulosics materials derived from nipah leaflet, nipah leaf stalk, oil palm leaflet and oil palm leaf stalk had been shown to possess high potential application in waste-water treatment as cheap and effective heavy metal ions adsorbents.

Key words: heavy metal ions, lignocellulosics materials, adsorption capacities, continuous column experiment

ABSTRAK

Logam berat seperti plumbum, kuprum dan nikel merupakan bahan yang bertoksik dengan mempunyai ketoksikan tinggi pada kepekatan rendah. Bahan lignoselulosik seperti anak daun nipah, tangkai daun nipah, anak daun kelapa sawit dan tangkai daun kelapa sawit telah digunakan sebagai bahan penjerap untuk larutan logam berat ini. Karbon teraktif juga telah digunakan sebagai bahan rujukan untuk perbandingan di bawah keadaan yang sama. Sampel daun yang berbeza telah menunjukkan variasi terhadap keupayaan bagi penjerapan ion plumbum, ion kuprum dan ion nikel. Karbon teraktif mempunyai penjerapan tertinggi terhadap ion plumbum (29.11mg/g) dan Ni^{2+} *(7.56mg/g). Sementara itu, anak daun kelapa sawit menjerap* Cu^{2+} *dengan paling efektif dan mempunyai keupayaan yang paling tinggi (9.80mg/g). keupayaan penjerapan bagi pelbagai sampel daun ini didapati adalah dipengaruhi oleh saiz partikel bagi penjerap, pH untuk larutan logam, kepekatan awal ion logam dalam larutan dan juga campuran larutan logam. Eksperimen kolum secara berterusan adalah sangat efektif dalam pengasingan logam berat. Hampir semua (>99%) daripada larutan logam berat telah diasingkan dengan menggunakan eksperimen ini. Bahan lignoselulosik diperoleh daripada anak daun nipah, tangkai daun nipah, anak daun kelapa sawit dan tangkai daun kelapa sawit mempunyai potensi tinggi dalam aplikasi perawatan air buangan sebagai penjerap ion logam berat yang murah dan efektif.*

Kata kunci: Ion logam berat, bahan lignoselulosik, keupayaan pejerapan, eksperimen kolum secara berterusan

CHAPTER 1

INTRODUCTION

Heavy metal ions such as mercury, lead, copper and nickel (Kumar & Dara, 1982) are toxic elements which have a relatively high density at low concentration (Zoek, 2004). It is metallic chemical element (Zoek, 2004) that always appears in industrial and mining waste waters (Morita *et al.*, 1987) and even in domestic wastewaters (Kumar & Dara, 1982).

Heavy metals cannot be degraded or destroyed. As trace elements, some of them are essential to maintain the metabolism of human body. However, if the concentrations of these heavy metals are too high, it can lead to poisoning. For instance, the sources of poisoning are drinking water contamination (lead pipes), high ambient air concentrations near emission sources or intake via the food chain (Zoek, 2004).

Zoek (2004) has also reported that heavy metal ions are bioaccumulative. It is very dangerous as when the chemical compounds entered the living organisms over time, the concentration of these chemical compounds will increase and higher than the chemical's concentration in the environment.

According to SenGupta (2002), the heavy metal ions always exist in different oxidation states in soil, water and air. Their reactivities, ionic charges and solubilities in water vary widely. In recent years, the removal of heavy metal ions from waste water has been investigated to prevent or minimize any possible health and pollution hazards to our environment (Seki *et al.*, 1997).

Heavy metal ions can be removed by using precipitation (as hydroxide, oxide, carbonate, sulphide), ion exchange, evaporation, freeze purification, reverse osmosis, electrolysis, cementation, flotation, adsorption (by clay and activated carbon), and electrodialysis (Kumar & Dara, 1982; Griffin *et al.*, 1977; Dean *et al.*, 1972). Each method has its merits and limitations in applications (Adeyiga *et al.*, 1998).

Activated carbon is a very effective adsorbent for the removal of heavy metal ions at trace quantities. But the process has not been used widely as it is very expensive (Adeyiga *et al.*, 1998). Therefore, there is a need to look into other alternatives to investigate a low-cost method which is effective and economical.

Lignocellulosics materials consist of combination of lignin and cellulose that strengthen woody plant cells. Seki *et al.* (1995) reported that lignocellulosics materials such as nut wastes (Friedman *et al.*, 1972; Waiss *et al.*, 1973; Randall *et al.*, 1976, 1977; Henderson *et al.*, 1977) tree leaves (Kimura *et al.*, 1986; Aoyama *et al.*, 1991; Watanabe and Kishi 1991; Saito *et al.*, 1992), barks (Masri *et al.*, 1974; Randall *et al.*, 1974; Henderson *et al.*, 1977; Fuji *et al.*, 1988; Aoyama *et al.*, 1993) and barley straw (Larsenand and Schierup 1981) are very effective heavy metal ions adsorbents.

According to Adeyiga (1998), the natural wastes such as tree leaves are very effective heavy metal adsorbents since they are inexpensive and highly available as alternative to existing commercial adsorbents. Many other materials have also been investigated, including microbial biomass, peat, compost, leaf mould, palm press fibre, coal, straw, wool fibre and rice milling by-products (Quek *et al.*, 1998; Wase and Forster, 19997; Singh and Rawat, 1997). However, Quek *et al.* (1998) also reported that not all of these materials are effective. Therefore, it is still important to identify other suitable low cost adsorbents for heavy metal removal from aqueous solutions.

The goal of this study is to find effective, abundant, renewable and cheap adsorbents for heavy metal ions in wastewater. If leaves of nipah and oil palms have been proven to be effective in heavy metal removal, they will play an important role in preserving environmental water quality.

1.1 Objectives of Study

The general objective of this study is to investigate the effectiveness of lignocellulosics materials derived from nipah (*Nypa fruticans*) and oil palms (*Elaeis guineensis*) in the removal of heavy metal ions from aqueous solutions. Among the specific objectives are:

1. Preparation and characterization of lignocellulosics materials derived from leaves of nipah and oil palms.

2. Determination of the adsorption capacities of various nipah and oil palms leave samples (leaflet and leaf stalk) for heavy metal ions.

3. Determination of factors affecting the removal efficiency and adsorption capacities of nipah and palm oil leaves for heavy metal ions. These factors include particle or mesh size, pH and initial metal ions concentrations.

CHAPTER 2

LITERATURE REVIEWS

2.1 Environmental and Health Effect of Heavy Metal Pollution

The industrial use of organic compounds containing metal additives in the petroleum and chemical industries such as textile mill products (Cr), organic chemicals (Cr, Pb), petroleum refining, pulp industries and fertilizers (Cr, Cu, Pb), iron and steel manufacturing plants (Fe) can lead to the production of non-ferrous metals, pigments and storage batteries, and metal processing, finishing and plating (Kumar & Dara, 1982) and these always cause heavy metal pollution to the environment (Inglezakis & Grigoropoulou, 2004).

2.1.1 Lead

Lead is one of the most dangerous trace elements as it is so widespread in our environment (Randall *et al.*, 1974) and bioaccumulative in living organism via the food chain. It can cause damage to the kidneys and has also been found to affect the nervous system and red blood cell (Brown *et al.*, 2000; Viessman and Hammer, 1993), cause problems in synthetic of hemoglobin, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system (Zoek, 2004).

2.1.2 Copper

Copper, at very low level, is a type of micronutrient which is an essential substance to human life (Zoek, 2004). However, when the concentration of copper is too high, it can cause stomach and intestinal irritation, liver and kidney damage and even anemia (Brown *et al.*, 2000; Gardea-Torresdey *et al.*, 1996). The sources of copper are mainly occurs in drinking water from copper pipes.

2.1.3 Nickel

Nickel is needed in producing red blood cells in human body when its concentration is low. However, in excessive amount with long term exposure, it can bring problems of heart and liver damage, decreased body weight and skin irritation (Zoek, 2004).

2.2 Heavy Metal Ions Removal from Wastewater

For reducing the concentration of the toxic elements such as cadmium and lead, precipitation of Cu^{2+} and Pb^{2+} as hydroxides from basic solutions has been used (Randall *et al.*, 1974). According to Seki *et al.* (1997), precipitation is the most inexpensive method for heavy metal removal. According to Randall *et al.* (1974), bacteriologically produced sulfide has been used by Pugsley *et al.* (1971) to precipitate heavy metal ions present in acid mine waters. However, this method is still not sufficient as it can only reduce the dissolved metal concentration to the solubility product level (Brown *et al.*, 2000; Patterson, 1989) and it can introduce undesirable waste sludge to our environment in large quantities (Seki *et al.*, 1997).

Wood- and non-wood based fibers have been found to have a significant sorption capacity for ionized copper, a heavy metal commonly found in stormwater. Research has been conducted in order to utilize the natural wood- and nonwood-based fibers in stormwater treatment. The current practice of stormwater filtration requires a large area. The problem is that it can be very expensive and typically does not solve the problem of fine suspended particles or dissolved pollutants. It is expected that with the integration of these fibers into a stormwater filtration system, not only its costs will be lower; it is biodegradable and can be regenerated for reuse (Han *et al.*, n.d.).

Morita *et al.* (1987) also reported that the utilization of chelating resins as substrates for removing heavy metal ions is very effective. However, it is still impractical as the costs of synthetic chelating resins are very high and their adsorption capacities are still low.

Dabrowski *et al.* (2004) reported that ion-exchange method is effective as the undesirable ions are replaced by others which do not contribute to contamination of the environment. It is technologically simple and enables efficient removal of even traces of impurities from solutions.

Zeolites are one of a family of hydrous aluminum silicate minerals, whose molecules enclose cations of sodium, potassium, calcium, strontium, or barium. These corresponding synthetic compounds are used chiefly as molecular filters and ion-exchange agents. According to Inglezakis & Grigoropoulou (2004), zeolites can be used to remove heavy metal ions (cadmium, lead, cobalt and nickel) from solutions using ion exchange method. For instance, clinoptilolite is one of the low cost zeolites that can be found easily (Inglezakis & Grigoropoulou, 2004). Insoluble starch xanthates are one of the useful methods for removing heavy metals from solutions (Kumar & Dara, 1982; Wing *et al.*, 1974, 1975).

Several inexpensive indigenous materials derived from naturally occurring lignocellulosics wastes have been studied for the utility as an adsorbent of heavy metals in wastewater. Vazquez *et al.* (1994) found that the bark was an effective adsorbent for removal of heavy metal ions from wastewater compared with other commercially available adsorbents. Besides, the cost of conducting the experiment was lower. Vazquez *et al.* (1994) has indicated that chemically modified *Pinus Pinaster* bark is effective in the adsorption of metal cations Zn^{2+}, Cu^{2+} and Pb^{2+} whereas Randall *et al.* (1976) also found that coastal redwood bark and black oak bark could be effectively removing heavy metal ions from solutions. Coniferous barks are also one of the effective adsorbents in removing heavy metal ions according to Seki *et al.* (1995).

Brown *et al.* (2000) has indicated that the peat can be used as an adsorbent for the capture of dissolved metals from waste streams. It is inexpensive and attractive as it can acts as an effective adsorbent for the removal of colloidal and dissolved metals. However, peat has poor physical characteristics that make it an unsuitable medium for the harsh environment of a full-scale industrial filter.

Orhan and Buyukgungur (1993) used adsorbents such as waste tea, Turkish coffee, exhausted coffee, nut and walnut shells to remove heavy metal ions from wastewater. They used batch studies and successfully showed that these adsorbents exhibit a good adsorption potential for Al(III) metal ions.

According to Quek *et al.* (1998), sago processing waste, which is both a waste and a pollutant, has been found effective in adsorbing lead and copper ions from aqueous solutions.

Larsen *et al.* (1981) investigated the feasibility of using various agricultural products and by-products such as barley straw for the removal of heavy metal ions from solutions. They had found that 1g of straw was able to adsorb amounts of Zn, Cu, Pb, Ni and Cd ranging from 4.3 to 15.2mg. The efficiency of the straw was improved by 10-90% when being mixed with $CaCO_3$.

Dupont *et al.* (2003) had evaluated the ion binding to solid organic matter. They used the NICA-Donnan model to remove the Cu(II), Pb(II) and Cd(II) using a lignocellulosics substrate extracted from wheat bran. This flexible and cheap substrate has been used as a natural filter to remove toxic metal ions. Moreover, such material also represents a very simple model of natural organic matter derived from lignin and cellulose.

2.3 Description of Oil Palms and Nipah

Oil palm (*Elaeis guineensis*) is the most rapidly expanding plantation crop in Sarawak which produces two distinct types of oils, palm oil and palm kernel oil (Purseglove, 1992). It appears tree like but it actually grows differently from hardwoods and conifers (Bergert, 2000; Thomas, 2000). Purseglove (1992) also reported that Malaysia is the main producer of palms oil. Oil palm plantations in Sarawak are located mainly in Sri Aman, Sibu and Miri Divisions (Johnson, 1991).

Nipah or nipa palm (*Nypa fruticans*) is an advanced palm where it grows on mud banks of brackish tidal rivers and is usually the dominant plant where it occurs (Purseglove, 1992). It is one of the mangrove plants which are commonly found in the coastal region of Sarawak (Johnson, 1991).

According to Johnson (1991), *Nypa* has many ethno-botanical uses. The mature nipah leaves are always used for palm-thatch and attap while the trimmed leaflet are used for making mats, baskets, bags, sun hats and umbrellas (Purseglove, 1992). Then, the surface tissue of young leaves can be stripped off to make the cigarette papers (Purseglove, 1992) or to wrap cooked rice (Johnson, 1991). The meat of the young nuts is fit to be eaten and the sap can be drunk as such, or used to make sugar (gula Melaka), alcohol or vinegar. Nipah sugar is produced mainly in the Kuching, Samarahan and Sri Aman Divisions of Sarawak (Johnson, 1991).

CHAPTER 3

MATERIALS AND METHODS

3.1 Sample Preparation

The samples (leaflet and leaf stalk of nipah and oil palms) were collected from the Asajaya Areas. Each sample was air-dried at about 40°C, cut into smaller pieces and ground in a Wiley mill to pass through 1 mm screen. Ground nipah and oil palms samples were separated by sieving using Endecott Test Sieve Shaker and labelled prior to their uses. Commercial activated carbon was examined as reference material for comparison purposes.

3.2 Physical and Chemical Characterisation of Nipah and Oil Palms Fibres

Physical Characterisation of Samples

Separation of fibers for each sample was done using the maceration process (Spearin and Isenberg, 1947). The ground samples were macerated with acetic acid and hydrogen peroxide. The samples were then be viewed under Scanning Electron Microscope and Projection Microscope for their physical characteristics such as fibre length, fibre width, lumen size and thickness of cell wall.

Chemical Characterisation of Samples

Chemical characterisation of oil palms and nipah leaves were carried out for moisture content, cold-water solubility, hot-water solubility and ash content according to the TAPPI standard methods.

3.3 Heavy Metal Ions Adsorption Study

The methods that had been used for metal ions adsorption are based on methods reported by Seki *et al.* (1997) with slight modification. The scope of this study had been limited to the adsorption of Pb^{2+}, Cu^{2+} and Ni^{2+} ions from aqueous solutions. According to Quek *et al.* (1998), two controls were used. A control without adsorbent was used to investigate whether the metal ions were adsorbed by or released from the wall of the beaker. Another control without metal ions (distilled water was used instead of metal solution) were used to estimate any leaching from adsorbents during the study period. The experiments were conducted in duplicate and the results were averaged.

3.3.1 Batch Equilibrium Experiments

The abilities of nipah and oil palms to adsorb heavy metal ions were determined in batchwise conditions using 1mM solutions of lead acetate, copper acetate and nickel acetate, separately. The pH of each solution was adjusted to the desired value with dilute HNO_3, or dilute NaOH solution. The test solution (100 ml) was added to the adsorbent

(0.5 g), and the suspension was shaken at room temperature (25°C) for various duration up to twenty-four hours. The adsorbent was then be filtered off and residual heavy metal ions in the filtrate were determined by atomic absorption spectrometry Perkin Elmer Model 3110 (AAS). The amount of heavy metal ions adsorbed by the adsorbent samples was calculated from the difference between the initial and final concentrations of the metal ions in solution.

3.3.2 Column Experiments

The ground samples were soaked into water for one hour and the resulting slurry was poured into a glass column (15 x 250 mm) fitted with a porous plug and a stopcock. After the adsorbent had settled, a wad of glass wool was placed on the top of the bed, and the liquid level run down to the top of the bed. Flow of the test solution through the column was controlled by the stopcock at the bottom of the column. The amount of Pb^{2+} in the column effluent was determined in the same manner described for the determination of heavy metal ions in the equilibrium experiments. The experiment was repeated with copper acetate and nickel acetate solutions of known concentrations.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Physical and Chemical Characterisation of Leaf Samples

4.1.1 Physical Characterisation

Up to 100 individual fibres of each macerated leaflet and leaf stalk were observed and measured using the projection microscope. Figure 4.1 to 4.4 show the morphological or physical characteristics of leaflet and leaf stalk of nipah and oil palm as observed under the projection microscope and scanning electron microscope.

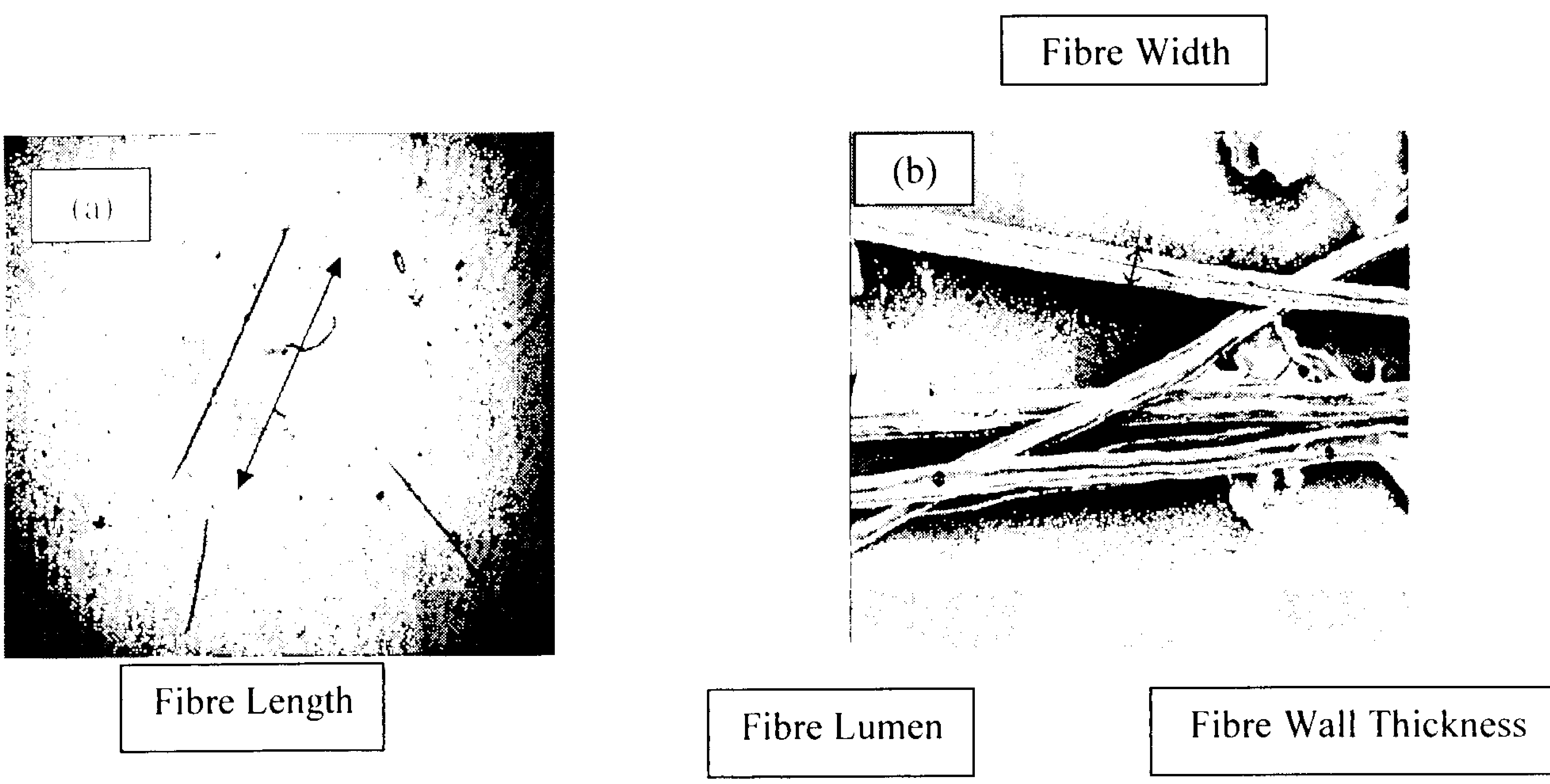

Figure 4.1: Nipah leaflet fibres as observed under (a) Optical microscope, (b) Scanning Electron Microscope (1000 x magnification)

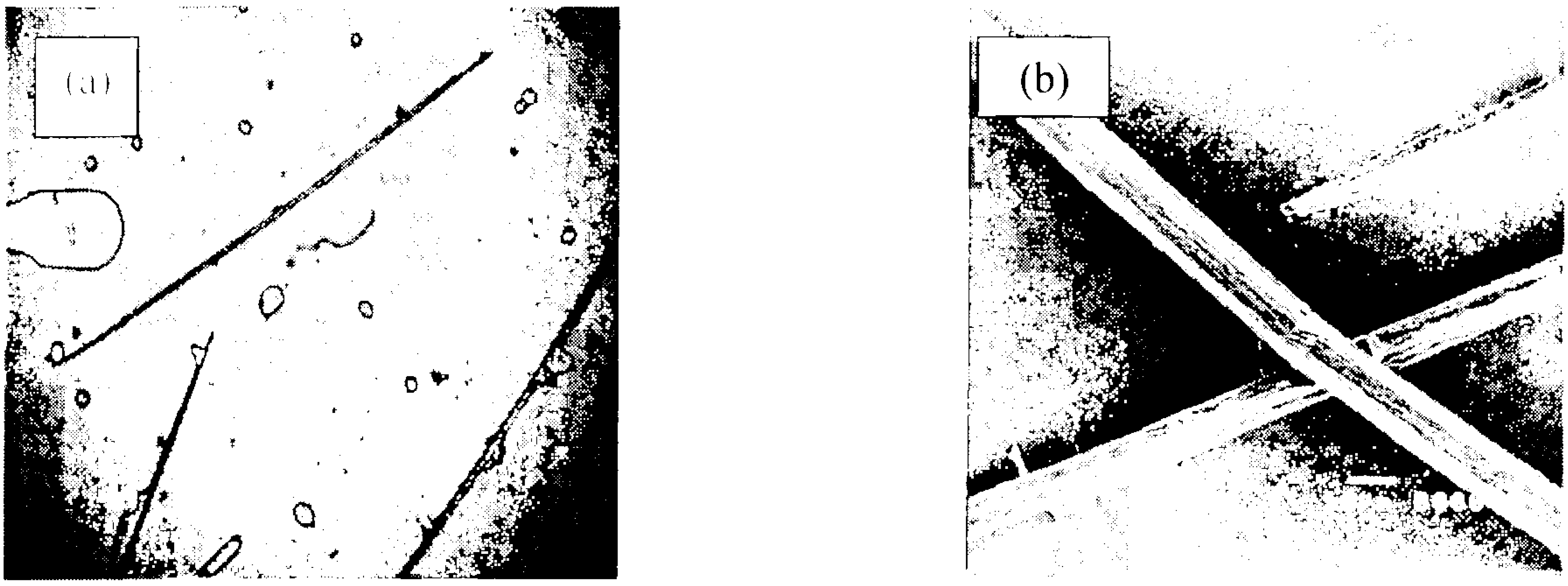

Figure 4.2: Nipah leaf stalk fibres observed under (a) Optical Microscope, (b) Scanning Electron Microscope (1000 x magnification)

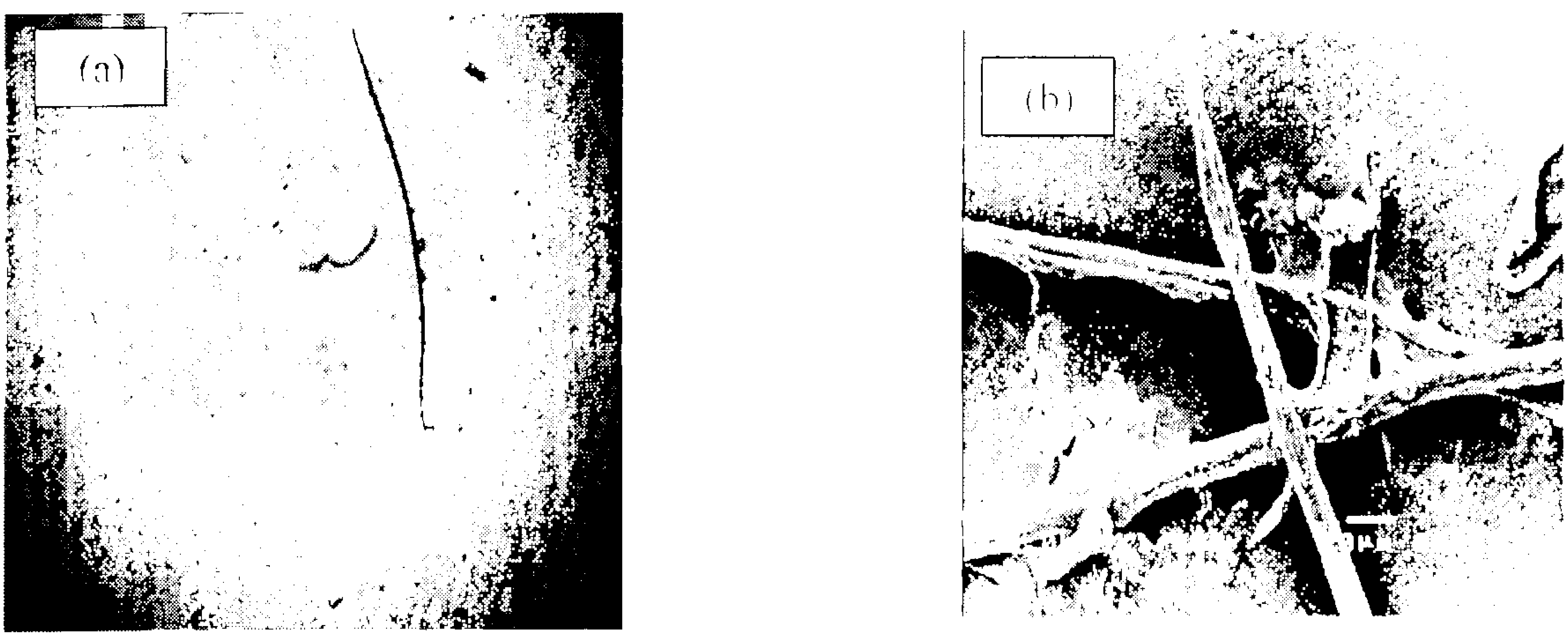

Figure 4.3: Oil palm leaflet fibres observed under (a) Optical Microscope, (b) Scanning Electron Microscope (1000 x magnification)

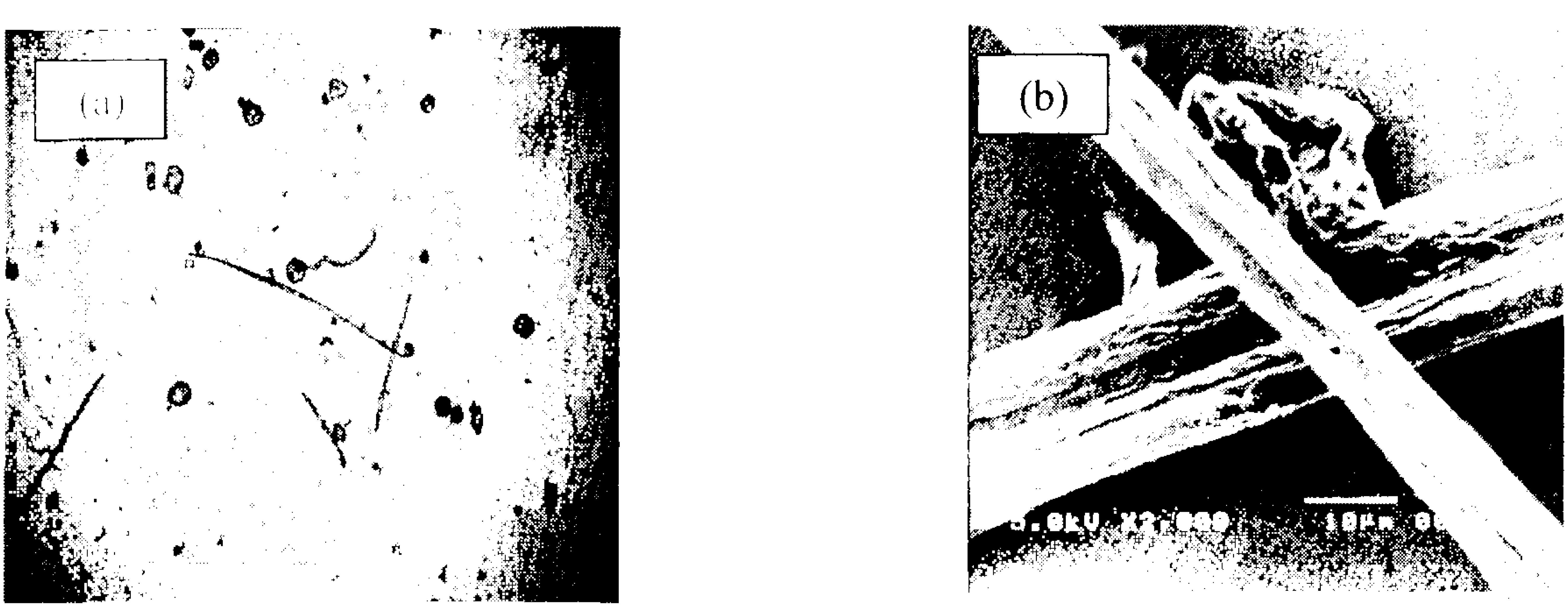

Figure 4.4: Oil Palm leaf stalk fibres observed under (a) Optical Microscope, (b) Scanning Electron Microscope (1000 x magnification)

Table 4.1 shows the physical characteristics of leaflet and leaf stalk samples of nipah and oil palms. All the leaflet and leaf stalk fibres were observed to be very similar morphologically. They only differed in their fibre length, width, lumen size and wall thickness. All leaf fibres were observed to possess heavily lignified walls. Among all of the leaf samples, nipah leaf stalk was observed to have the longest mean fibre length (1216.50 µm) whereas the mean fibre length of oil palm leaflet was the shortest (762.80 µm). The length of nipah leaf stalk fibres ranged between 450-2435 µm. Oil palm leaf stalk had the widest fibre width (18.65 µm) whereas those of nipah leaflet and leak stalk and oil palm leaflet were quite similar at about 14.50 µm. Besides, oil palm leaf stalk also had the largest lumen size (11.30 µm) and thickest fibre wall (4.20 µm). Oil palm leaflet was observed to have the smallest lumen size (9.60 µm) whereas nipah leaflet had the thinnest wall of 3.23 µm.

Table 4.1: Physical Characteristics of nipah leaflet, nipah leaf stalk, oil palm leaflet and oil palm leaf stalk samples

Physical Characteristics		Nipah Leaflet	Nipah Leaf Stalk	Oil Palm Leaflet	Oil Palm Leaf Stalk
Fibre Length (µm)	Range	205.00-1160.00	450.00-2435.00	200.00-1720.00	175.00-1650.00
	Average	764.60±204.70	1216.50±439.29	762.80±325.60	856.50±330.04
Fibre Width (µm)		14.45±4.54	14.50±4.17	14.75±3.44	18.65±4.60
Fibre Lumen (µm)		10.90±4.46	10.30±3.47	9.60±3.31	11.30±3.88
Fibre Wall Thickness (µm)		3.23±1.14	3.58±1.24	3.45±1.22	4.20±1.25

The surfaces of the fibres are normally irregular and such irregularity contributed larger surface area of the fibres. This characteristic would increase the tendency of the adsorbents to bind with heavy metal ions as these surfaces are hydrophilic in nature.

According to Timell (1995), the primary function of the fibres is to provide mechanical support to the tree. Fibres are being classified into two types: libriform fibres and fibre tracheids. Fibres contribute 30-75% of the wood volume. Normally, both libriform fibres and fibre tracheids are present in the same species. Libriform fibres have small, slitlike or dot-like pits. The pits are always simple or with inconspicuous borders. Normally, they are scarce and occur commonly scattered over the fibre wall. Fibre tracheids exhibit conspicuous bordered pits, which are larger and more abundant than libriform fibres, and tend to be in vertical lines (Timell, 1995). Besides, fibre tracheids can also participate in conduction.

Timell (1995) had also reported that the maximum length of vessel elements in oil palm (*Elaeis guineensis*) is approximately 4.0 mm and its maximum width is about 300 μm. Oil palm had been observed to have rounded and thick-walled parenchyma cells. It has some special features such as extremely large vessel elements and scalloped fibre walls.