



CHAPTER II

REVIEW OF THEORETICAL BACKGROUND AND LITERATURES

2.1 Electrospinning

Electrospinning is a fiber spinning technique that produces polymer fibers of nanometer to micrometer range in diameters. In the electrospinning process, a polymer solution held by its surface tension at the end of a capillary tube is subjected to an electric field. Charge is induced on the liquid surface by an electric field. Mutual charge repulsion causes a force directly opposite to the surface tension. As the intensity of the electric field is increased, the hemispherical surface of the solution at the tip of the capillary tube elongates to form a conical shape known as the Taylor cone. When the electric field reaches a critical value at which the repulsive electric force overcomes the surface tension force, a charged jet of the solution is ejected from the tip of the Taylor cone. Since this jet is charged, its trajectory can be controlled by an electric field. As the jet travels in air, the solvent evaporates, leaving behind a charged polymer fiber which lays itself randomly on a collecting metal screen. Thus, continuous fibers are laid to form a non-woven fabric (Doshi, 1995).

The formation of fibers from this spinning process can be divided into two parts:

2.1.1 The Initiation of the Jet

Before the electric field is applied to the polymer solutions, and when the capillary tube are in a vertical position and carries a drop at the tip of nozzle, the relation between the surface tension and the height of the column of liquid under equilibrium conditions is given by

$$2\gamma(1/R + 1/r) = \rho gh \quad (2.1)$$

where γ is the surface tension of the liquid of density ρ , h is the height of the column of liquid above the lowest surface of the drop, R is the radius of

curvature of the liquid at the upper liquid surface and r is the radius of curvature of the liquid at the lower surface of the liquid (Michelson, 1990).

Consider a droplet of polymer solutions that is applied to a high electric field. Charges that flow onto liquid surface repel each other. The repulsion forces are opposed to the forces from surface tension. The polymer droplet becomes unstable when the charges distributed on the surface overcome the surface tension. The conditions that are necessary for a charged surface to become unstable are described by considering the equilibrium equation,

$$V^* = (4 \pi r \gamma)^{1/2} \quad (2.2)$$

where V^* is the critical potential, r is the droplet radius, and γ is the surface tension of the solutions (Kooombhongse, 2001). For the droplets subjects to a higher potential, $V > V^*$, the droplet elongates into a cone-like shape that was described mathematically by Taylor and often referred to as a Taylor cone (Taylor, 1969).

As the potential is increased, which obtain the maximum instability of the liquid surface, a jet of liquid ejected from the tip of the cone. Taylor showed that the critical voltage V_c (expressed in kilovolts) at which the maximum instability develops is given by

$$V_c^2 = 4H^2/L^2 (\ln 2L/R - 1.5)(0.117\pi R\gamma) \quad (2.3)$$

where H is the distance between the electrodes, L and R are the length and radius of the capillary, respectively, and γ is the surface tension.

2.1.2 The Continuous Flow of the Jet

The mechanism of the appearance of a stable electrospinning jet is evidently established by the observation of the jet formation through the high speed electronic camera which recorded up to 2000 frames per second with a time resolution of approximately 0.0125 ms (Reneker, 2000).

There are two kinds of electrical forces that act on the jet: the external field that tries to pull the jet toward collector and the self-repulsion between the charges carried by adjacent segments of the jet that try to push each other apart. The

self-repulsion can also cause different types instability such as bending instability and splitting instability.

In bending instability, or whipping instability, the jet rotates in a conical region, whose vertex is the end of the straight jet. The other end of the jet, which is highly stretched, and reduced in diameter, is deposited on the collector as a result of the fast whipping motions (Shin, 2001).

After some time, segment of a loop suddenly developed a new bending instability, but at a smaller scale than the first. Each cycle of bending instability can be described in three steps (Reneker, 2000).

Step (1) A smooth segment that was straight or slightly curved suddenly developed an array of bends.

Step (2) The segment of the jet in each bend elongated and the array of bends became a series of spiraling loops with growing diameters.

Step (3) As the perimeter of the loops increased, the cross-sectional diameter of the jet forming the loop grew smaller; the conditions for step (1) were established on a smaller scale, and the next cycle of bending instability began.

The schematic drawing of the electrospinning process is shown in figure 2.1.

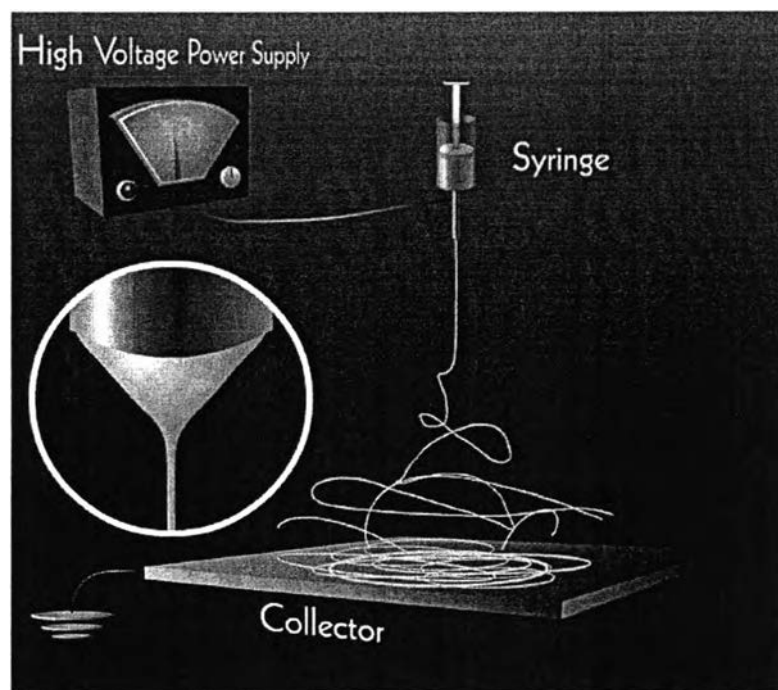


Figure 2.1 Schematic drawing of the electrospinning process (Dan, 2004).

The other instability of the charged jet is the splitting instability. It occurs when the charge density of the charged jet increases as the solvent evaporates. The charged jet can reduce its charge per unit surface area by ejecting a smaller jet from the surface of the primary jet, or by splitting apart to form two smaller jets (Koombhongse, 2001).

2.1.3 Applications of Electrospun Fibers

Due to the high surface area to volume ratio, high porosity, and light weight of the electrospun fibrous mats, a number of applications have been sought out (Jayaraman, 2004).

2.1.3.1 Scaffolds for Tissue Engineering

Almost all of the human tissues and organs have fibrous network to provide mechanical integrity to them. These tissues and organs are, for examples bone, dentin, collagen, cartilage, and skin. Due to similarity in the structure, electrospun fibers are easily found to be prospective materials to be used as templates for tissue scaffold applications, controlled release fibers for wound dressing, pharmaceutical, and cosmetic applications. For the treatment of injured or defective tissues or organs, biocompatible materials are designed and fabricated to form structure that mimic the structure and biological functions of extracellular matrix (ECM). Human cells can attach and organize well around the fibers that are smaller than them. As a result, nanometer or sub-micrometer fibrous scaffolds could be suitable template for cell seeding, migrating, and proliferating. It has been reported that scaffolds having high surface area to mass ratio (ranging from 5 to 100 m²/g) is efficient for fluid absorption and dermal delivery (Huang, 2003).

2.1.3.2 Protective Clothing

Protective clothing for military personnel is expected to help maximize the survivability, sustainability, and combat effectiveness of soldiers against extreme weather conditions, ballistics, and nuclear, biological, and chemical warfare. So a lightweight, breathable fabric, permeable to both air and water vapor, insoluble in all solvents, and highly reactive to chemical agents, is desirable. Polymer nanofibers had been developed for various protective clothing applications. It was found that compared with conventional textiles, electrospun nanofiber mats

provide minimum impedance to moisture vapor diffusion and maximum efficiency in trapping aerosol particles.

2.1.3.3 Reinforcement in Composite Materials

Publications on nanofiber-reinforced composite materials are limited in the literature because of the difficulty of producing these fibers. However, their higher surface-to-volume ratio may improve the interlaminar toughness and interfacial adhesion in nanofiber-reinforced composites.

2.1.3.4 Sensors

Polymer nanofibers have been used in the development of functional sensors possessing high sensitivity due to the high surface area of nanofibers. Polymer used in this applications were poly(lactic acid-*co*-glycolic acid) and poly(acrylic acid)-poly(pyrene methanol).

2.1.3.5 Drug Delivery System

Controlled delivery systems are used to improve therapeutic efficiency and safety of drugs by delivering them a rate dictated by the need of the physiological environment over a period of treatment to the site of action (Kenawy, 2002). The advantages of the electrospun fibers over the convention cast film are the electrospun fiber has higher surface area and high porosity than film resulting in minimization of the initial burst release of drug and higher amount of drug release was obtained.

2.1.3.6 Filters

Filtration is a necessary process in various engineering applications. Filtration efficiency or capture efficiency of filter media has been shown to be inversely proportional to the diameters of the fibers in filters. Because of the very high surface area-to-volume ratio and the resulting high surface cohesion of nanofibers, tiny particles on the order of less than 0.5 μm are easily trapped in the nanofiber mats.

2.1.3.7 Ultra-thin layer chromatography stationary phase

The layers are sufficiently stable for general use without the need for a binder and were prepared in sizes from 2 to 3 cm wide and 6 cm long for separations. The devices have been shown to decrease time of analysis and volume of solvent needed while vastly increasing the efficiency of the analysis.

2.2 Polyacrylonitrile

2.2.1 Properties of Polyacrylonitrile

Polyacrylonitrile (PAN), a synthetic resin prepared by the polymerization of acrylonitrile. A member of the important family of acrylic resins, it is a hard, rigid thermoplastic material that is resistant to most solvents, slow to burn, and of low permeability to gases. Most polyacrylonitrile is produced as acrylic and modacrylic fibre, a common substitute for wool in clothing and home furnishings.

Acrylonitrile ($\text{CH}_2=\text{CHCN}$) is obtained by reacting propylene ($\text{CH}_2=\text{CHCH}_3$) with ammonia (NH_3) and oxygen in the presence of catalysts. It is a flammable liquid that is highly toxic if ingested and is a known carcinogen; strictly regulated procedures are required for its handling and disposal. Acrylonitrile monomers (single-unit molecules) are suspended, almost always in combination with other monomers, as fine droplets in water and are induced to polymerize to PAN through the action of free-radical initiators. General properties of PAN are shown in Table 2.1.

Table 2.1 General properties of polycrylonitrile fiber

Properties	Details
Repeating Unit	$-\left[\text{CH}_2 - \underset{\substack{ \\ \text{C} \equiv \text{N}}}{\text{CH}} \right] -$
Glass transition temperature:	85°C.
Melting temperature:	317°C.
Amorphous density at 25°C:	1.184 g/cm ³
Molecular weight of repeat unit:	53.06 g/mol.

PAN has none of the hazardous properties of the monomer. Owing to the formation of strong chemical bonds between the nitrile (CN) groups, the polymer molecules resist most organic solvents and do not melt without decomposing. In

most cases the polymer is dissolved in special solvents and spun into acrylic fibres, which are defined as fibres that contain 85 percent or more of PAN. Because PAN is difficult to dissolve and is highly resistant to dyeing, very little fibre is produced containing PAN alone. On the other hand, a copolymer containing 2 to 7 percent of a vinyl comonomer such as vinyl acetate can be solution-spun readily to fibres that soften enough to allow penetration by dyestuffs. Acrylic fibres are soft and flexible, producing lightweight, lofty yarns. Such properties closely resemble those of wool; hence, the most common use of acrylics in apparel and carpets is as a wool replacement—for example, in knitted wear such as sweaters and socks. Acrylics can be sold at a fraction of the cost of the natural fibre, and they offer better sunlight resistance, mildew resistance, and resistance to attack by moths. Acrylic fibres are also used as precursors for the production of carbon and graphite fibres, as replacements for asbestos in cement, and in industrial filters and battery separators.

Acrylics modified by halogen-containing comonomers such as vinyl chloride or vinylidene chloride are classified as modacrylics. (By definition, modacrylics contain more than 35 percent and less than 85 percent PAN.) The presence of chlorine imparts a notable flame resistance to the fibre—an advantage that makes modacrylics desirable for products such as children's sleepwear, blankets, awnings, and tents. However, they are not as widely used as the simple acrylics because of their higher cost and because they are somewhat prone to shrinkage in clothes dryers.

Although the polymerization of acrylonitrile had been known since the 1890s, commercial production of PAN fiber did not begin until the 1940s, after Ray C. Houtz of E.I. du Pont de Nemours & Company (now DuPont Company) discovered spinning solvents that could dissolve the polymer. DuPont introduced its trademarked Orlon acrylic fiber in 1948; Orlon was soon followed by the Monsanto Chemical Company's Acrilan, American Cyanamid's Creslan, Courtaulds' Courtelle, and others. The decade of the 1950s also saw the introduction of modacrylics such as Eastman Kodak Company's Verel and Monsanto's SEF.

2.3.2 Electrospinning of Polyacrylonitrile Fiber

In 2006, Sutasi-promprae *et al.* have prepared ultrafine electrospun polyacrylonitrile fibers. PAN solutions in dimethylformamide (DMF) in various

concentrations ranging from 2.1 to 17.4 wt% to investigate the effects of some solution properties (i.e., solution concentration, viscosity, surface tension, and conductivity) on morphological appearance and diameters of the obtained fibers. The concentration, and hence the viscosity, of the spinning solutions significantly affected the morphology and diameters of the as-spun PAN fibers. The applied electrostatic field strength and nozzle diameter slightly affected the diameters of the as-spun fibers, while the emitting electrode polarity did not show any influence over the morphology and size of the as-spun fibers. Utilization of the rotating-drum collector enhanced the alignment of the as-spun fibers. Within the investigated concentration range, the average diameter of the fibers ranged between 80 and 725 nm.

Li *et al.*(2007) prepared electrospun polyacrylonitrile nanofibrous membranes for lipase immobilization. The concentration of the PAN solution in DMF, the flow rate of the PAN solution, the applied voltage, the solution flow rate, and the distance between needle tip and collector were controlled at 8% (w/w), 1.5 ml/h, 20.0 kV, and 20.0 cm, respectively. Long uniform PAN nanofibers with diameter ranging from 150 to 300 nm were electrospun from an 8% (w/w) PAN solution in DMF.

To prevent the formation of beads and/or beaded nanofibers, Zhou *et al.* (2009) developed the spinning solution by adding 5 wt.% acetone and 0.01 wt.% dodecylethyldimethylammonium bromide into 10 wt.% PAN solution in DMF. The PAN solutions were electrospun at a positive voltage of 20 kV, a tip-to-collector distance of 22 cm, and a solution flow rate of 1.5 mL/h. The result shows uniform electrospun PAN nanofibers with diameter of ~330 nm.

Another solvent system for the electrospinning of PAN nanofibers was studied by Kurban *et al.* (2010). PAN solutions were made by mixing PAN powder (150,000 g mol.wt.) in >99.5% purity dimethylsulphoxide (DMSO) in varying concentrations in the range 2–10 wt.% PAN . Sodium chloride (NaCl) and the anionic surfactant 4-styrenesulphonic acid, sodium salt hydrate (SASH), were added to some solutions at concentrations of 1 and 5 mg ml⁻¹, respectively, to investigate their effects on polymer morphology and diameter. A voltage between 5 and 10 kV was adjusted. The solution flow rate and the distance between needle tip

and collector were controlled at 300 ± 10 mm and $200 \mu\text{l} / \text{h}$. Within the investigated concentration range, the average diameter of the fibers ranged between 60 and 380 nm.

2.3 Heavy Metal Removal

2.3.1 Conventional Metals Precipitation Treatment

Conventionally, precipitation has been the method most often used to remove heavy metals which is shown in Figure 2.2. Of the few precipitation methods, hydroxide and sulfide are the two main methods currently used, and hydroxide precipitation is by far the most widely used method. However, this method does not ensure total compliance for the various metals present in the waste stream, since all metal hydroxides do not completely precipitate at a single pH. Theoretical hydroxide precipitation curves for metals normally found in plating baths are shown in Figure 2.3. The graph indicates that there is no one ideal pH for a multiple-metal system.

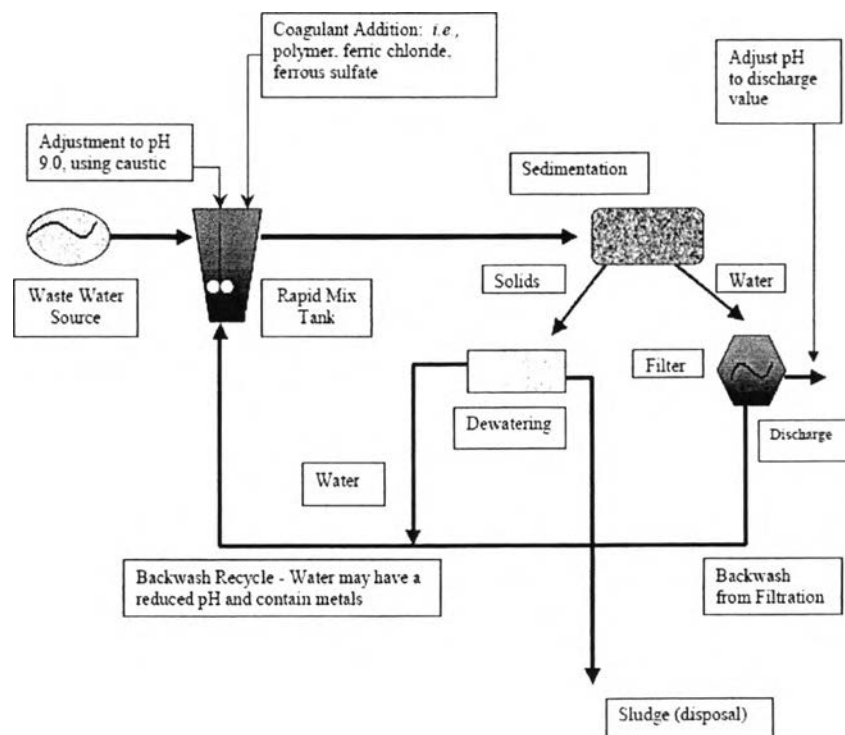


Figure 2.2 The processes of a conventional metals precipitation treatment plant

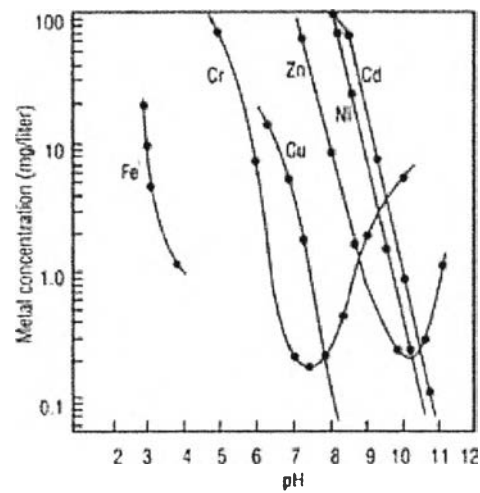


Figure 2.3 Precipitation of heavy metals as hydroxides

In practice, hydroxide precipitation is generally carried out at the best compromised pH for metals in the waste stream, normally between 8.5 - 9.5. Therefore, achievable concentrations may not meet discharge requirements. Additionally, the presence of chelating or complexing agents, oil and grease, synergistic reactions and high concentrations of dissolved solids can result in diminished efficiency of hydroxide precipitation.

2.3.2 Ion Exchange

Ion exchange is an adsorption process in which charged molecules, called ions, in a solution are exchanged for other ions on the surface of an adsorbent or resin. Ion exchange only removes compounds that ionize. It is also a concentration process. The phenomenon of ion exchange occurs in special synthetic resins and in many natural solids. A synthetic resin can be visualized as a skeleton-like structure having many exchange sites.

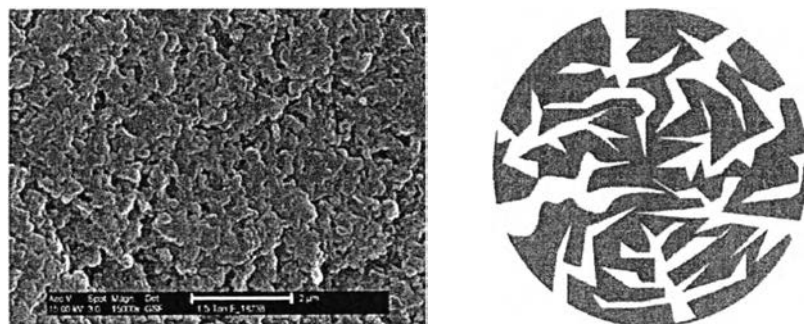


Figure 2.4 Ion exchange resin beads contain many fine pores that fill with water

This skeleton is insoluble in water, but is electrically charged holding ions of opposite charge at the exchange sites. Exchangers with negatively charged groups are called cationic and attract positive ions (dissolved metals such as nickel). Anion exchangers are positively charged and attract negative ions (anions such as chlorides, sulfates and chromates). Most ion exchange resins currently in use are made from a styrene divinylbenzene copolymer, appropriately treated to graft the functional groups. The copolymer is then treated by a process called sulfonation which produces the cation resins. Ion exchange resins are classified as strongly or weakly acidic cation exchange resins and strongly or weakly basic anion exchange resins (Dr Stefan Neumann and Phil Fatula, 2009).

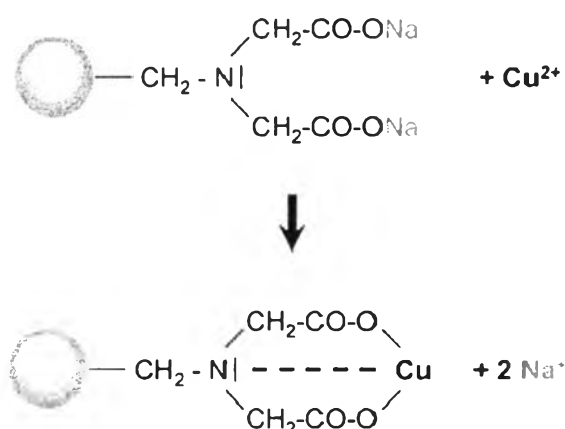


Figure 2.5 Mechanism of binding of a copper-cation to the functional group of an imino-di-acetic acid-resin (IDA-resin)

2.3.3 Chelating Materials

Chelating materials are used to treat plating wastewater to remove heavy metals remaining after neutralization and coagulating sedimentation, or to collect metal ions by adsorption from wastewater. Surface complex formation and chelation have often been considered as the important adsorption mechanisms for heavy metal ions on various adsorbents. It has been reported that adsorbents containing nitrogen on the surface (i.e., with amino, hydrazine, thioamide, and imidazoline groups) facilitate metal ion adsorption through the chelation mechanism. In particular, the amino group on an adsorbent has been found to be one of the most effective chelating groups for adsorption or removal of heavy metal ions from

aqueous solutions. Hence, there has been considerable interest in surface modification to introduce useful functional groups on the surface so as to enhance the adsorption capability of the fibers for removing heavy metal ions.

Table 2.2 Adsorption capacities of Cu(II) on various adsorbents

Adsorbent	Physical form	pH	Q_{\max} (mg g ⁻¹)	Ref.
Poly(N,N-dimethylaminoethyl methacrylate)	Powder	5.5	31.46	Zhu et al.
Magnetic Chitosan	microspheres	5	19	Podzus et al.
Poly(hydroxyethyl methacrylate)	nanobeads	5	61.4	Türkmen et al.
N,N-di(carboxymethyl) dithiocarbamate	Resin	5	1.57 ^a	Jing et al.
Polyacryloamidoxime	Fiber	5	1.12 ^a	McComb
hydrolyzed polyacrylonitrile	Fiber	4.5	29.64	Deng et al.
Aminated Polyacrylonitrile	Fiber	4.5	31.45	Deng et al.
Poly(acryloamidino diethylenediamine)	Fiber	4.8	4.49 ^a	Ko et al.
Polyacrylamidoxime	nano fiber	n/a	52.7	Saeed et al.

n/a: not available

^a: The unit is mmol g⁻¹

2.4 Planar Chromatography

Chromatography is a physical method of separation in which the components to be separated are distributed between two phases, one of which is a stationary phase over which the other mobile phase moves in a specific direction. Planar chromatography is a mode of chromatography in which the stationary phase is spread on a flat, planar surface. TLC is an important planar chromatographic technique that is widely used as a cost-effective method for rapid analysis of simple mixtures. It requires minimum sample cleanup as it uses a disposable stationary phase and has a high sample throughput because of its ability to analyze several samples in parallel. It allows greater flexibility and simplicity in sample evaluation because of the possibility of sequential detection by complementary techniques, postchromatographic derivatization for identification and quantification, archiving a

separation for evaluation at a later time, and accessibility of the sample because of the planar format. It can be applied to samples where analyte lack a convenient chromophore making detection by other methods difficult and can be applied for analyzing samples with minimal prepurification. In some respects, the techniques of TLC and HPLC are complementary. Optimum resolution in TLC is obtained when R_f is about 0.25, and it is interesting to note that this corresponds to a retention factor of 3.0, which is in the optimal range found for column. Liquid chromatographic column methods provide better efficiencies, better mass-transfer properties and higher operating velocities. HPLC can also be fully automated making this method more popular for most analytical applications. By contrast, TLC is the most popular method because of its low cost, simplicity, and flexibility.

2.4.1 High Performance Thin Layer Chromatography (HPTLC)

High performance thin layer chromatography is an enhanced form of thin layer chromatography (TLC). A number of enhancements can be made to the basic method of thin layer chromatography to automate the different steps, to increase the resolution achieved and to allow more accurate quantitative measurements.

Automation is useful to overcome the uncertainty in droplet size and position when the sample is applied to the TLC plate by hand. One recent approach to automation has been the use of piezoelectric devices and inkjet printers for applying the sample (Morlock et.al, 2010).

The spot capacity (analogous to peak capacity in HPLC) can be increased by developing the plate with two different solvents. After the plate is exposed to the first solvent, the solvent is removed; the plate is rotated 90° and developed with a second solvent. If the two solvents show different selectivity, then the spots may be spread over the entire surface of the plate. This is obviously a form of two-dimensional chromatography (Nurok, 1989).

2.4.2 Theoretical Considerations

2.4.2.1 *Separation Efficiency*

Velocity constant is dependent on external factors including saturation level of vapor phase in contact with the stationary phase. It is also related to the properties of the mobile and stationary phases by the equation

$$\kappa = 2K_0 d_p (\gamma / \eta) \cos \theta \quad (2.4)$$

where K_0 is the permeability constant, d_p is the average particle diameter, γ is the surface tension of the mobile phase, η is the viscosity of the mobile phase, and θ is the contact angle. Assuming a uniform particle size distribution, the velocity constant increases linearly with the average particle size and thus the solvent front velocity is greater for coarse-particle layers. For silica gel layers, the contact angle for all common solvents is close to zero as all solvents wet it adequately. For reversed phase layers containing bonded, long-chain alkyl groups the contact angle of the solvent increases rapidly with increasing water content of the mobile phase. At about 30–40% (v/v) water, $\cos \theta$ becomes smaller than 0.2–0.3 (Wall 2005).

To improve solvent compatibility, modern reversed-phase TLC plates are prepared from large-size particles (10–15 μm) or from sorbents with a defined degree of modification that is lower than that of exhaustively silanized sorbents. Consequently, solvent with high viscosity and surface tension will migrate at much slower rate than that with low viscosity and surface tension. It is therefore advantageous to mix solvents with low κ values with those with higher values to improve migration rate, but care will need to be exercised to ensure that the solvents are miscible and that the appropriate polarity is maintained (Poole and Poole, 1989).

2.4.2.2 Partition Coefficient

Various components of the mixture are thus retarded in proportion to their interaction with the adsorbent. At any given time, a particular analyte molecule is either in the mobile phase, moving along at its velocity, or in the stationary phase and not moving at all in the downstream direction. The ratio of the equilibrium concentration of an analyte in the stationary phase divided by its equilibrium concentration in the mobile phase is described by the distribution constant K_a and is represented by the equation;

$$K_a = C_s / C_M \quad (2.5)$$

where C_S is the concentration of the analyte in the stationary phase and C_M is its concentration in the mobile phase. It is this ratio that controls the rate of migration of an analyte. For an ideal situation, the ratio of C_S to C_M will follow a linear correlation. However, if the spot/band is overloaded, the relationship of C_S to C_M becomes nonlinear. Overloading of sample usually results in a slight increase in R_f value. This increases with loading concentration. Nonlinear curves are undesirable because they not only cause the R_f value to vary but also can impair critical separations because of “tailing” effects and introduce unnecessary errors in quantification.

2.4.2.3 Retention/Retardation Factor

The position of any solute spot in TLC is characterized by its retention/retardation factor R_f . It is a fundamental qualitative value and is expressed as;

$$R_f = \frac{\text{Distance travelled by the analyte } (Z_s)}{\text{Distance travelled by the solvent front } (Z_f)} \quad (2.6)$$

R_f values range from 1.0 for analyte migrating to the solvent front to 0.0 for an analyte strongly retained at the point of application (Figure 2.6). It is sometimes more convenient to report as $R_f \times 100$. The reproducibility of R_f values depends on many factors, such as quality of the sorbent, humidity, layer thickness, development distance, and ambient temperature (Sherma and Fried, 2003).

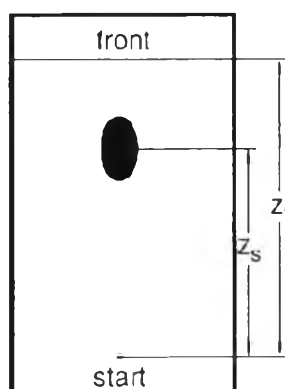


Figure 2.6 The thin-layer chromatographic parameters used in calculation of R_f

2.4.2.4 Capacity Factor

The capacity factor of a substance is defined as “the ratio of its retention time in the stationary phase to that in the mobile phase.”

$$k = t_s / t_m \quad (2.7)$$

This is the simplest and most fundamental formulation of the qualitative chromatographic behavior of a substance that measures the degree of retention. A measurement of capacity factor will help to determine whether retention shifts are due to the stationary phase (capacity factor is changing with retention time changes) or due to the mobile phase (capacity factor remains constant with retention time changes).

2.4.2.5 Spot Capacity

In quantitative chromatography, the separation number is defined as the highest possible number of completely separated substances, between $k = 0$ and $k = 10$. Two substances are completely separated, when the distance between the two adjacent peak maxima and the sum of both peak widths at half-peak height are same. It thus measures the efficiency of separation. Separation number is a quantity measurable with sufficient accuracy, simple, relatively independent of the chromatographic technique, easy to handle, and suitable for comparison and optimization. Separation number is given by the expression;

$$SN = (Z_f / b_0 + b_1) - 1 \quad (2.8)$$

Z_f = migration distance of the front

b_0 = extrapolated width of the spot at $R_f = 0$

b_1 = extrapolated width of the spot with $R_f = 1$

In a TLC densitogram, widths are measured at half-height. A typical capillary controlled HPTLC has a separation number of 10–20 while a capacity of 40–80 is possible for forced-flow TLC.

2.4.2.6 Plate Height

The most common measure of the efficiency of a chromatographic system is the plate number originally called the number of theoretical plates contained in the chromatographic column system. Broadening of a chromatographic spot can be simply expressed in terms of the theoretical plate number N of the given chromatographic system:

$$N = 16 Z_f Z_s / W_s \quad (2.9)$$

where, Z_f and Z_s are the migration lengths of the mobile phase and solute, respectively, and W_s is the chromatographic spot width in the direction of the mobile phase migration. N can also be calculated by the equation:

$$N = 16(Z_s/W_s)^2 \quad (2.10)$$

The calculation of plate number based on this equation is demonstrated in Figure 2.7. Although the numerical values of N obtained for different solutes on the same chromatographic plate coincide fairly well, they usually differ significantly for another plate type. For this reason, the quantity N can be regarded as

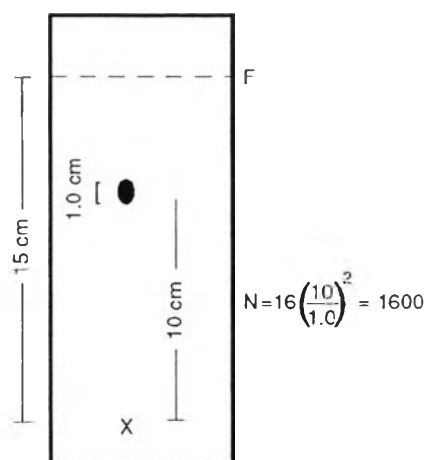


Figure 2.7 Calculation of plate number, X=origin, F=solvent front

an approximate measure of the separating efficiency of chromatographic plates. It is proportional to the migration length of the mobile phase Z_s , such that, when Z_s/W_s ratio remains constant, an increase in Z_f results in an increase of N and better separation. This proportionality of N and Z_f is given by the relationship

$$N = Z_f/H \quad (2.11)$$

where H is the so-called HETP value (i.e., height equivalent of a theoretical plate). The quantity H , or simply the plate height, measures the efficiency of a given chromatographic system per unit length of the migration distance, Z_f , of the mobile phase. Small H values mean more efficient chromatographic systems and large N values. The main goal of efforts to enhance performance of thin layers is the attainment of small H values and maximum N values. As in other chromatographic techniques, the efficiency of a given TLC system is better (i.e., H is smaller) for smaller particles of stationary phases or supports, lower mobile-phase flow rates, less-viscous mobile phases, and smaller solute molecules (Fried and Sharma, 1999).

2.4.2.7 Resolution

The main goal of chromatography is separation of constituents in a mixture. Chromatographic spots of two adjacent solutes may, however, overlap to a smaller or greater degree in many cases. The separation between two spots

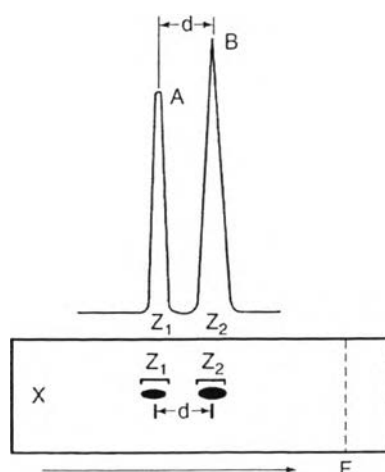


Figure 2.8 Chromatographic resolution determined from spot or densitometric scan.

is measured by the quantity R_s , and is called resolution (Miller 2005). The R_s of two adjacent chromatographic spots 1 and 2 is defined as being equal to the distance between the two spot centers divided by the mean spot widths (Figure 2.8)

$$R_s = z_2 - z_1 / 0.5(w_1 + w_2) \quad (2.12)$$

The quantity R_s serves to define separation. When $R_s = 1$, the two spots are reasonably well separated. R_s values larger than 1 indicates better separation while smaller than 1 suggest a poor separation. Spot overlap becomes more disturbing when the concentration of solute in one spot is much greater than that in the other.

2.4.2.8 Selectivity

Selectivity of separation is seldom referred to in the case of thin-layer chromatography, although no serious reason can be given for avoiding this term. To the contrary, selectivity of separation is a useful chromatographic notion, no matter which particular technique, column or planar, is being considered. In the case of thin-layer chromatography, the separation factor α can be defined as $\alpha = K_1/K_2$ which remains in full conformity with the definition used for the column technique. Several options for increasing α are available, and these can be ranked in order of decreasing impact; change in mobile-phase composition, change in mobile-phase pH, change in stationary phase, change in temperature, and special chemical effects.

2.5 Applications of Electrospun Polycrylonitrile Nano Fiber Matrices

2.5.1 Functionalized Polyacrylonitrile for Heavy Metal Ions Removal

Woven polyacryloamidoxime cloth was prepared from the polyacrylonitrile precursor via reaction in methanolic hydroxylamine by McComb and Gesser(1997). Preparation was controllable and reproducible and the reaction conditions were optimized with respect to the time of conversion, the concentration of $\text{NH}_2\text{O}\cdot\text{HCl}$, and the temperature of conversion. The cloth produced had a large capacity for Cu(II) and Pb(II) of 71.2 and 450 mg g^{-1} (1.12 and 2.17 mmol g^{-1}) respectively.

In 2001, Chang *et al.* produced a new poly(acrylphenylamidrazone phenylhydrazide) chelating fiber is synthesized from polyacrylonitrile fiber and used for preconcentration and separation of trace Ga(III), In(III), Bi(III), V(V) and Ti(IV) from solution (5–50 ng ml⁻¹ Ti(IV) or V(V) and 50–500 ng ml⁻¹ Ga(III), In (III) or Bi(III) in 1000–100 ml of solution can be enriched quantitatively by 0.15 g of fiber at a 4 ml min⁻¹ flow rate in the pH range 5–7 with recoveries >95%).

After that, in 2002, they synthesized Poly(acryldinitrophenylamidrazone-dinitroacrylphenylhydrazine) chelating fiber from polyacrylonitrile fiber and used for enrichment and separation for traces of Au(III), Ru(III), In(III), Bi(III), Zr(IV), V(V), Ga(III) and Ti(IV) ions from solution samples. The results show that 10–100 ng ml⁻¹ of Au(III), Ru(III), In(III), Bi(III), Zr(IV), V(V), Ga(III) and Ti(IV) ions can be quantitatively enriched by the chelating fiber at a 2 ml min⁻¹ of flow rate in the range pH 4–5, and desorbed quantitatively with 20 ml of 5 M HCl for In(III), Bi(III), Zr(IV), V(V), Ga(III), Ti(IV) and 20 ml of 4 M HCl+2% CS(NH₂)₂ solution for Au(III), Ru(III) (with recovery 95%).

The surface of polyacrylonitrile fiber (PANF) was modified through a simple hydrolysis process in a sodium hydroxide solution by Deng *et al.* (2003). The hydrolyzed polyacrylonitrile fiber (HPANF) possessed conjugated sequences of –C=N– on the surface and was much more effective in removing copper ions from aqueous solution than the PANF that contained the –C≡N groups. The amount of copper ion adsorption onto the HPANF increased with solution pH values in the pH range of 2–6 studied. The maximum adsorption amount (q_m) of copper ions by the HPANF is predicted as 29.64 mg/g.

Ko *et al.* (2004) used fourier transform infrared (FT-IR) spectroscopy to study the effect of pH on anion and cation adsorption onto poly(acryloamidino diethylenediamine). The polymer was synthesized through the coupling of diethylene triamine with polyacrylonitrile fiber in the presence of AlCl₃ 6H₂O addition. The adsorption capacity of this polymer was 11.4 mequiv/g. The ions used for the adsorption test were CrO₄⁻², PO₄⁻³, Cu²⁺, Ni²⁺, Fe²⁺, and Ag⁺. At low pHs, only ionic bonds existed, whereas at high pHs, no bonds existed. However, in the middle pH region, both ionic bonds and hydrogen bonds formed between poly(acryloamidino diethylenediamine) and the chromate ion or phosphate ion. When

poly(acryloamidino diethylenediamine) and metal ions (Cu^{2+} , Ni^{2+} , Fe^{2+} , and Ag^+) formed complexes, a hydrogen-bonding effect was not observed with Fourier transform infrared. The quantity of metal ions adsorbed onto poly(acrylo-amidino diethylenediamine) followed the order $\text{Ag}^{2+} > \text{Cu}^{2+} > \text{Fe}^{2+} > \text{Ni}^{2+}$.

In 2008, Saeed *et al.* prepared amidoxime-modified polyacrylonitrile (PAN-oxime) nanofibers for metal adsorption. PAN nanofibers (prepared by an electrospinning technique) were chemically modified with amidoxime groups. The adsorption of the amidoxime-modified PAN (PAN-oxime) (25% conversion) nanofibers followed Langmuir isotherm. The saturation adsorption capacities for Cu(II) and Pb(II) of 52.70 and 263.45 mg/g (0.83 and 1.27 mmol/g), respectively, indicating that the monolayer adsorption occurred on the nanofiber mats. In addition, over 90% of metals were recovered from the metal-loaded PAN-oxime nanofibers in a 1 mol/L HNO_3 solution after 1 h.

2.5.2 Use as Stationary Phase for Thin-Layer Chromatography

In 2009, Olesik *et al.* used electrospinning technique to produce PAN nanofibers use as the stationary phase for thin layer chromatography. The devices use a nanofibrous stationary phase with fiber diameters that are 400 nm. Separations of mixtures of laser dyes and mixtures of steroidal compounds were performed to illustrate the capabilities of these UTLC media. The complete analyses were found to require very little development time and require less solvent than typical TLC methods. The efficiency of the separations was substantially improved compared to that determined using commercial phases.

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