CHAPTER 1

INTRODUCTION

Heavy metal pollution is an important environmental problem due to its toxic effects and accumulation throughout the food chain. The main sources of heavy metal pollution are mining, milling and surface finishing industries resulting to discharging a variety of toxic metal ions such as Pb(II), Cd(II), Cu(II) and Cr(III) into the environment.[1]

Unlike organic pollutants, heavy metals cannot be degraded or readily detoxified biologically. The distribution, chemical and physical properties of the above four heavy metals included its toxicity are summarized in Tables 1.1-1.4.

Industry and commerce are feeling the impact of tighter legislation relating to the discharge of polluted water to the environment because of the increasing cost of pollution monitoring, control and elimination. So, there are demands for cheaper method of aqueous effluent treatment. One of the methods is the use of sorbents to adsorb metals under suitable conditions. Then the sorbents will be filtered out and the treated water becomes clean.

Sorbents are divided into two types, i.e. synthetic sorbent and biosorbent. Recently, biosorbents such as seaweeds are extensively used because of their low cost, high capacity and wide range of benefit.

In order to understand how biosorbent works, the theory of metal adsorption is illustrated briefly.

Table 1.1 Distribution, properties and toxicity of cadmium

Distribution[2-4]	Relatively low concentrations in the environment. (natural waters < 1 µg/l, soils and seawater 0.04-0.30 µg/l) but high concentration originating from anthropogenic activities (sewage sludge > 100 mg/kg and topsoil 1-69 mg/kg). Production: 90% cadmium oxide, others: cadmium sulfide, cadmium chloride etc. Usage: coating and plating 35%, batteries 25%, pigments 20%, plastic and synthetic products 15% and other uses 5%.
Properties[3,5]	Atomic number = 48, atomic weight = 112.41, electronegativity = 1.69, atomic radius = 148.9 pm, density = 8650 kg/m^3, oxidation state +2, crystalline form as a close packed hexagonal, silver-white. Chloride form: soluble in water, neutral and toxic. Oxide form: non- soluble in water, neutral and toxic.
Toxicity[3,4]	Inhalation (mainly) and oral, average oral intake10-70 µg/day Exposure to organ: kidney, liver, lung (~10-40%) and pancreases. Abnormality: renal dysfunction, hypertension, hepatic injury, lung damage after inhalation exposure, reproductive toxicity, teratogenic effects and bone defects.

Table 1.2 Distribution, properties and toxicity of chromium

Distribution[3,4]	Ubiquitous in the atmosphere, biosphere, hydrosphere and crust of the earth. Average concentration: 100 ppm in crust rocks, 0.5 ppb in sea water, 1 ppb in stream waters, 0.23 ppm in land plants and 1 ppm in marine plants. Major source: chromite($FeOCr_2O_3$) naturally occurring ore, found with FeO or MgO. Usage: alloying metals 60%, chemicals 15%, others 25%
Properties[3,5]	Atomic number = 24, atomic weight = 51.99, electronegativity = 1.66, atomic radius = 124.9 pm, density = 7190 kg/m^3, oxidation states -2 to +6. Color: metallic silver-white Chloride form: soluble in water and neutral. Oxide form: soluble in water but slightly soluble in acid.
Toxicity[3,4]	Order of exposure to organ: lung> gastrointestinal tract> skin. Conversion form in human: Cr(III) can be converted to Cr (VI) by an oxidation process which occurs externally from human's body. Among oxidation states of Cr, Cr(VI) is the most toxic and easily found in nature. Intake dosage: dietary intake (ESADDI), 50 to 200 micrograms per day. Overt signs: perforation of the nasal septum, skin ulcers, and liver and kidney damage. Acute poisoning: tissue necrosis and severe kidney loss.

Table 1.3 Distribution, properties and toxicity of copper

Distribution[4]	Ubiquitous in the atmosphere, biosphere, hydrosphere and crust of the earth. Average concentration: 50 ppm in continental crust, 10-40 ppm in sandstones, 30-150 ppm in shales, 20-300 ppm in marine black shales. Average concentration in natural ore: 140 ppm (as elemental state, sulfides, arenites, chlorides and/or carbonates). Usage: building wire and copper tube 28%, copper cable and power utilities 18%, in-plant equipment 12%, automotive equipment and ship building 13% and household products 15%.
Properties[3,5]	Atomic number = 29, atomic weight = 63.55 electronegativity = 1.90, atomic radius = 127.8 pm, density = 8960 kg/m^3, oxidation states: +1, +2 and +3 the most stable oxidation state is +2. Chloride form: soluble in water, neutral and slightly toxic. Oxide form: non- soluble in water, neutral and slightly toxic. Color: metallic brown-red.
Toxicity[3,4]	Inhalation (mainly) and oral, average oral intake10 mg/day. Intake dosages: 2 mg (dust) Exposure to organ: lung, liver and kidney. Abnormality: vomiting, hemolysis, liver and kidney damage.

Table 1.4 Distribution, properties and toxicity of lead

Distribution[3,4]	Natural source: galena or (PbS), the silvery metallic compound of lead and sulphur. It's characteristics are sparkle and broken ore. Stable isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb Usage: batteries 80.8%, oxides in ceramics and glass 3.0% ammunition 4.7% paint 0.5% and other uses 9.2%.
Properties[3,5]	Atomic number = 82, Atomic weight = 207.20, electronegativity = 2.33, atomic radius = 175 pm, density = 11350 kg/m^3, melting point 327.5 °C, oxidation state +2 and +4 but +2 is the most stable one. Color: gray-white Chloride form: poor soluble in water, neutral and toxic. Oxide form: poor soluble in water, neutral and toxic.
Toxicity[3,4]	Order of exposure: Oral > inhalation (as dust) > skin Intake dosage: (by oral) 6 mg/kg children, (by oral) 55 mg/kg adult, (by inhalation) 1 μg/m^3 air. Effect to: enzyme systems, heme synthesis Symptoms: gastrointestinal disturbances, anemia, insomnia, weight loss, motor weakness, muscle paralysis and nephropathy. Least toxic concentration: 1.11-3.50 mg/l blood

1.1 Theory of Adsorption[6,7]

Adsorption phenomena are operative in most natural physical, biological, and chemical systems. Adsorption operations employing solids such as activated carbon and synthetic resins are widely used in industries and for purification of water and wastewater.

The process of adsorption can be explained by its definition: the accumulation of substance(s) at the surface of another. By the different of phases, the adsorbing phase is the adsorbent, and the substance adsorbed at the surface of that phase is adsorbate. It is different from absorption, which is a process of transferring substance (s) from one phase to another.

Sorption processes are illustrated graphically by the phase partitioning relationships shown in Figure 1.1. The terms C_e and q_e represent the equilibrium concentrations of substance in each of two contiguous phases. Typically q_e is the amount of adsorbate (mg/g) and C_e, the residual concentration of adsorbate in the fluid phase from which it has been partially removed. Curves I and III indicate the nonlinear relationship characteristic of favorable and unfavorable adsorptions, respectively. Curve II represents the linear separation pattern characteristic of adsorption and absorption.

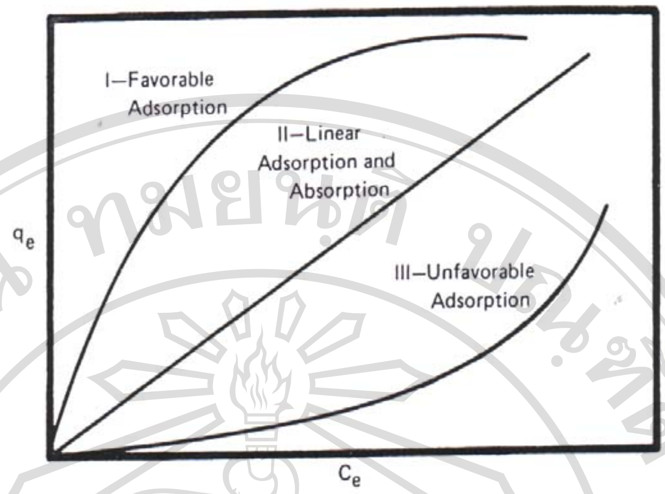

Figure 1.1 Type of equilibrium sorption separations; q_e = amount sorbed and C_e = amount in solution[6]

A quantitative equilibrium distribution among phase concentrations is defined for each combination of a specific adsorbate, adsorbent, and system conditions. The character of the distribution affecting a specific adsorption process is dependent on an adsorbate, adsorbent and adsorption system.

The adsorption process represented by curve I in Figure 1.1 is most suitable for process applications such as water treatments because this favorable adsorption exhibits other than partitioning of certain solutes of interest with several matrices between the adsorbent and the liquid phase matrices during separations and do not lend those matrices to the efficient separations. Although this adsorption type is favorable, it cannot be explained sufficiently in all factors. The time required to achieve equilibrium must also be factored into the selection and design of practical adsorption process.

Although curve II represents the linear adsorption pattern characteristic of absorbent. It is the amount sorbed in solution with constant rate. This curve is consistent with conditions in which the number of adsorption sites remains constant throughout the concentration range. When the new sites occurred and conversed the former layer, the available surface will be expanded proportionally to the amount of solute adsorbed.

Curve III is unfavorable adsorption for sorbate at very low concentration, this is due to the low adsorption affinity of the adsorbate to the adsorbent. Increasing the solute concentration leading to the greater adsorption affinity of the solute to the adsorbent and hence, the amounts of solute adsorbed were occurred. Therefore, the amounts of solute adsorbed increase rapidly as the solubility limit of adsorbate is approached.

Principles of phase partition equilibrium and the rate of operation are based on type of interactions, type of interfaces and matrix(s) interactions to the surface of sorbent. The character of adsorption is considered in terms of thermodynamics and mass transport process. Methods for quantifying adsorption equilibrium can be represents as models.

1.2 Adsorption Principles [6,7]

1.2.1 Surface interactions

Adsorption at a surface is resulted from binding forces between the individual atoms, ions, or molecules of an adsorbate and the surface, all of these forces having their origin in electromagnetic interactions. Surface adsorption may be categorized into four types, namely exchange, physical, chemical and specific adsorptions.

Exchange adsorption or ion exchange involves electrostatic attachment of ionic species to sites of opposite charge at the adsorbent surface, with subsequent displacement of these species by other ionic adsorbate of greater electrostatic affinity. Physical adsorption results from the action of Van der Waals forces, which are comprised of both London dispersion forces and classical electrostatic forces. Chemical adsorption involves a reaction between an adsorbate and an adsorbent resulting in a change in the chemical form of the adsorbate. The resulting chemisorptive bond is usually stronger than that derived from the physical Van der Waals forces. Attachment of adsorbate molecules at functional groups on adsorbent surfaces can also result from specific interactions which do not result in adsorbate transformation. These interactions, designated "specific adsorptions," exhibit a range of binding energies ranging from values commonly associated with physical adsorption to the higher energies involving in chemisorption. The net dispersion, electrostatic, chemisorptive, and functional group interactions broadly define the affinity of an adsorbent for a specific adsorbate.

Adsorption also relates to certain properties of the adsorbate relative to the solution phase, notably those of surface tension and solubility. For example, many organic compounds can effectively lower the surface tension of water and the energy balance of aqueous systems of such compounds favors their partitioning to solid-water and gas-water interfaces. The extent of adsorption is greatly influenced by the solvophobicity or lyophobicity of a compound. The tendency of an adsorbate to be adsorbed from solvent at interfaces with other phases is great when increasing solvophobicity with respect to a given solvent. Bonding between substances and solvents in which it is dissolved must be broken before adsorptions occur.

Adsorption from solution onto a solid can occur as a result of one or both of two characteristic properties for a given solvent-adsorbate-adsorbent system. The primary driving force may relate to the solvophobic or lyophobic character of the adsorbate or to adsorbate-adsorbent affinity. Several factors, i.e. adsorbate, adsorbent and system affect adsorption. For the adsorbate, concentration, molecular weight, molecular size, molecular structure, molecular polarity, steric form or configuration, and the nature of background or competitive adsorbates are considered. In the case of adsorbent, the most important parameters are capacity and rate process including surface area, the physicochemical nature of the surface, the availability of that surface to adsorbate molecules or ions, the physical size and the form of the adsorbent particles. System parameters such as temperature and pH can also markedly influence adsorption.

1.2.2 Adsorbate-solvent properties

A relationship between the adsorption of a substance from a solvent and its solubility in that solvent can be generally anticipated. For example, the water solubility of organic compounds within a particular chemical class decreases with increasing molecular size or weight due to long hydrocarbon chain. Thus, adsorption from aqueous solution increases as a homologous series is ascended. Molecular size can affect adsorption rates if these are controlled by intraparticle diffusive mass transport within porous adsorbents, which generally is rapid for a small molecule. It must be emphasized that the rate dependence on molecular size can be generalized only within a particular chemical class or homologous series. Large molecules of one chemical class may adsorb more rapidly than smaller ones of another if higher energies or driving forces for adsorption are involved.

A polar solute from a non-polar solvent will be strongly adsorbed onto a polar adsorbent, and vice versa. Solvation by water, for example, involves formation of a hydrogen bond between the positive hydrogen atoms of water and a negative group on a solute. Water solubility is thus expected to increase with increasing polarity, and it shows that adsorption from aqueous solution generally decreases as polarity increases.

Adsorption reactions are normally exothermic, with changes in enthalpy of the order of those for condensation or crystallization reactions. The equilibrium adsorption in a given system is thus generally found to increase with decreasing temperature. Conversely, the rate of approach to equilibrium normally increases with increasing temperature. This is because adsorption kinetics are generally controlled by diffusive mass transfer.

1.2.3 System properties

The adsorption of other ions may thus be influenced by solution pH because of interaction between hydrogen, hydroxide ions and adsorbents. The extent to which adsorption differs between the conjugate forms of acidic or basic compounds, pH affects adsorption in that it governs degree of protolysis or "ionization" of such compounds. In the case of neutral species (e.g., acetic acid and phenol molecules), they tend to adsorb more strongly from the aqueous phase than do their corresponding ionic forms.

The components of a mixture of adsorbates may mutually enhance adsorption, act relatively independently, or interfere with one another. In such effects, the adsorption depends on the kinetic of adsorption. The reduction of both adsorption capacities and adsorption rates can be expected if the affinities of the adsorbates do not differ by orders of magnitude or there are no specific interactions among them. This can explain that the adsorption of more than one substance generally reduces the surface sites available to other. For diffusion controlled rates of adsorption by porous adsorbents, very slowly diffusing species in mixed adsorbate systems can suppress rates of uptake of those which diffuse more rapidly.

1.3 Adsorption Equilibrium

The adsorption of a substance from one phase to the surface of another in a specific system leads to a thermodynamically defined distribution of that substance between the phases when the system reaches equilibrium. The common manner in which to depict this distribution is to express the amount of substance adsorbed per unit weight of adsorbent, q_e, as a function of the residual equilibrium concentration, C_e, of substance remaining in the solution phase. An expression of adsorption isotherm defines the functional equilibrium distribution of adsorption with adsorbate concentration in solution at constant temperature. Commonly the amount of adsorbed material per unit weight of adsorbent increases with increasing concentration, but not in direct proportion, as illustrated by the isotherm depicted in Figure 1.1 (Curve I)

Experimental isotherms are useful for describing adsorption capacity to facilitate evaluation of the feasibility of this process for a given application, for selection of the most appropriate adsorbent, and for preliminary determination of adsorbent dosage requirements. The isotherm can be used in prediction of modeling procedures for design the adsorption systems. An additional usefulness is for theoretical evaluation and interpreting of thermodynamic parameters, such as heat of adsorption. Several equilibrium models have been developed to describe adsorption isotherm relationships.

1.3.1 Langmuir model[8,9]

Langmuir proposed theory to describe the adsorption of gas molecules onto metal surfaces. The Langmuir adsorption isotherm has been successfully applied to many sorption processes including the adsorption of aqueous onto solid phase. A basic concept is that sorption takes place at specific sites, within the adsorbent and that once adsorbate molecule occupies a site, no further adsorption can take place at the same site. As a result, a saturation value is reached beyond which no further sorption can take place. The formation of monolayer at equilibrium can then be represented by the expression:

$$q_e = \frac{Q^0 bC_e}{1 + bC_e} \qquad (1.1)$$

Where q_e is the amount of solute adsorbed per unit weight of adsorbent, Q^o is the solid phase concentration corresponding to complete coverage of available sites,

C_e is the residual liquid phase concentration at equilibrium and b is the adsorption constant. Equation1.1 can be written in a variety of linear forms to facilitate fitting experimental data for parameter evaluations as illustrated in equation 1.2 and 1.3.

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \qquad (1.2)$$

$$\frac{1}{q_e} = \frac{1}{Q^0} + \frac{1}{bQ^0 C_e} \qquad (1.3)$$

1.3.2 Freudlich model[8,9]

Freudlich studied the sorption of a material onto animal charcoal. He demonstrated that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of the solute in the solution was not a constant at different solution concentrations. The Freudlich expression is an empirical equation based on sorption on a heterogeneous surface. Hence the empirical equation can be written as follows:

$$q_e = K_F C_e^{1/n} \qquad (1.4)$$

Where K_F is the Freudlich constant and n is the Freudlich exponent. A linear form of the Freudlich expression is

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (1.5)$$

If the adsorption data followed the Freudlich isotherm then plotting log q_e versus log C_e would give straight line. The values of K_F and n could be calculated from intercept and slope, respectively. These parameters are indicative the capacity and the intensity of adsorption.

1.4 Biosorption of Heavy Metals by *Sargussum* Species[10]

Sargassum is a genus of brown algae that has given its name to the Sargasso Sea, where it is found in great abundance. It is a type of seaweed that name commonly used for the multicellular marine algae. It can be classified into various types. All of those types contain the same structure of polysaccharide ester with very rich of hydroxy groups. The rich hydroxy polysaccharide structure shows the capability of ion adsorption. Most of them are used as a biological adsorbent.

There has been an intense research effort aimed at characterizing the metal binding properties of various forms of biomass such as seaweed. Metals uptake by *Sargassum* species were summarized in Table 1.5.

As shown in Table 1.5, the metal uptake values were tabulated from experimental data acquired sufficiently high initial metal concentrations so that the maximum uptake (corresponding to the q_{max} of the Langmuir isotherm) was achieved. It can also be seen that the pH at which the maxima were achieved is not the same for all heavy metals, as would be expected on the basis of the varying metals affinity for the acidic functional groups (i.e. carboxylic and sulfonic).

1.4.1 *Sargassum polyceratium* characters

Sargassum polyceratium is growing by attaching marine's crust. It erects from a rather irregular disklike holdfast and reaching the lengths of 4.5-9.0 dm. It has strong numerous lateral branches which finally producing short-spur branches. The branches of all degrees generally abundantly and muriculate. The less branches often nearly smooth, or smooth in the older portions. The stem leaves are at first on the main axes. The later axes are closely set on the spur branches. It can characterize with one margin toward the axis. Its lanceolate is more typically broadly ovate with the lengths of 1.5-3.5 cm. It has a long base with the length of 5-10 mm. The base is broad, sessile, and the asymmetrical base is very broadly rounded or even transverse. Its apex is broadly obtuse to rather acute. Its margin is dense and deep called dentate-serrate and has a length of 2-6 mm. It has long receptacular branches with axillary style. Other branches are short and forking and not densely massed or conspicuous.

Up to the limitation of available, *S. polyceratium* can be easily found in Thailand. This species of *Sargassum* have never been used and applied in the adsorption experiments. In terms of economics, usage of the available material is the advantage. This research work is therefore focused on the use of *S. polyceratium* as a biological adsorbent for heavy metals, i.e., Pb(II), Cu(II), Cd(III) and Cr(III).

Table 1.5 Uptake of metals by different *Sargassum* species[11]

Metal	Species	pH	Metal uptake (mg/g)
Cd	*Sargassum natans*	3.5	56.16
	Sargassum vulgare	4.5	37.92
	Sargassum fluitans	4.5	34.08
	Sargassum muticum	4.5	32.64
	Sargassum filipendula	2.5	31.68
Cu	*Sargassum vulgare*	4.5	26.97
	Sargassum filipendula	4.5	25.81
	Sargassum fluitans	4.5	23.20
Au	*Sargassum natans*	2.5	160.37
Fe	*Sargassum fluitans*	4.5	25.74
Ni	*Sargassum fluitans*	3.5	21.00
	Sargassum vulgare	3.5	2.52
Pb	*Sargassum natans*	3.5	100.04
	Sargassum vulgare	3.5	90.20
Zn	*Sargassum fluitans*	4.5	35.40

The study of metal adsorption can be achieved by differentiating the initial and remaining amount of metals. After the metal uptake by an adsorbent, the residual quantity exists at low level that can be determined by an appropriate method. In this work, two commonly sensitive techniques for metal determination namely atomic absorption spectrometry (AAS) and inductively coupled plasma – optical emission spectrophotometry (ICP-OES) are employed.

1.5 Inductively Coupled Plasma Optical Emission Spectroscopy [12]

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is a major technique for elemental analysis. The sample to be analyzed, if solid, is normally first dissolved and then mixed with water before being fed into the plasma. Atoms in the plasma emit light (photons) with characteristic wavelengths for each element. This light is recorded by one or more optical spectrometers and when calibrated against standards the technique provides a quantitative analysis of the original sample.

1.5.1 Apparatus

The apparatus for the ICP-OES is composed of three main sections: the nebulizer, the torch and the detection system (Figure 1.2).

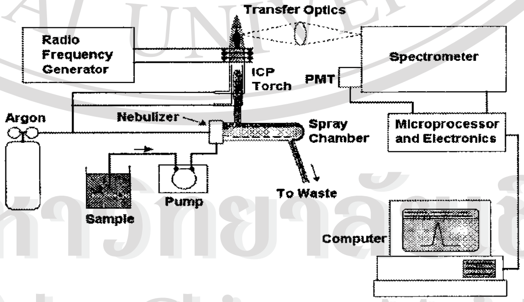

Figure 1.2 ICP-OES schematic diagram[12]

1.5.1.1 Plasma

The primary component of the Inductively Coupled Plasma- Optical Emission Spectroscopy (ICP-OES), is the plasma source, which is formed and maintained using a torch and a load coil. Plasma is defined as anything that contains >1% electrons and positive ions in mixture, conducts electricity and is affected by a magnetic field. Because of these properties, plasma can be safely produced and contained using electric and magnetic fields.

In the ICP-OES, plasma is formed above the torch, which is composed of three concentric tubes of a glass or quartz. The innermost tube provides nebulizer flow of the sample into the plasma, the middle tube, called the intermediate gas flow, prevents the plasma from getting too close to the nebulizer flow, and makes nebulizer injection easier. The outer tube, called the outer flow, provides argon gas for initial plasma ignition, as well as keeping the load coil cool from the immense heat.

The load coil consists of a liquid-cooled conductive metal, which provides an alternating current of 700 to 1500 watts oscillating at 27 or 40 MHz. This current sets up an annular magnetic field region within the coil and above the torch, where the plasma is maintained. Ignition of the plasma occurs by first swirling argon gas in the outer flow, then producing a magnetic field within the load coil. An electrode produces a spark, which strips some electrons from the argon atoms. Electrons are confined within the magnetic field, and collides with other argon atoms. Plasma is created by a chain reaction which ionizes argon atom within the magnetic field. An argon cross flow which shears the top of the plasma further confines its expansion (Fig. 1.3). A notch on the torch side provides an emission viewing window for the detector.

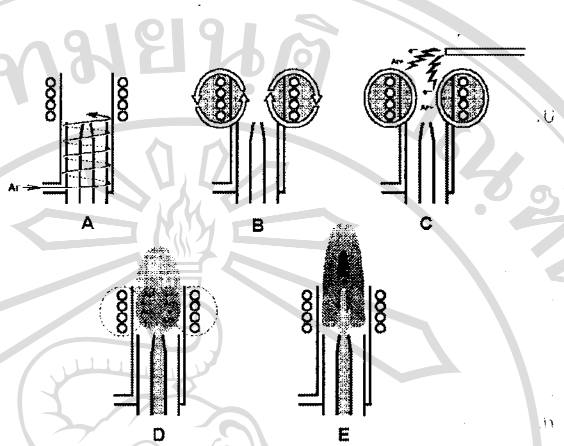

Figure 1.3 Ignition sequence for plasma: argon gas is swirled though torch (A) RF coil produces magnetic field for containment (B) electrode provides seed electrons (C) ionization of argon (D) and formation of plasma (E)[12]

Ionization process are carried out. The region at the base of the plasma, closest to the nebulizer flow, is called the preheating zone (PHZ). This region is involved in dessolvation of the aerosol, The plasma contains various regions where different steps of the leaving the salt form of the analyte. Vaporization of the salt then produces a gas phase, which is then atomized. The initial radiation zone (IRZ) and the normal analytical zone (NAZ) are involved in the excitation and radiation of the sample. A toroidal region at the base of the plasma is formed by the puncture of nebulized sample, called the inductive region (IR).

1.5.1.2 Nebulizer

The ICP-OES operates by introducing an aqueous sample into an energy source, which is plasma in this case. The sample is picked up by a peristaltic pump, and passed through a nebulizer, using inert argon gas as a carrier. This reduces the liquid sample to a fine aerosol, which is more effectively ionized by the plasma. Various types of nebulizers are available, including cross-flow, concentric, Babbington, and its variations. Although the resulting mists of these nebulizers generally contain small and consistent droplets, the nebulized samples are passed through a spray chamber, which filter out larger droplets to ensure consistency. The aerosol is then injected through the torch and into the plasma for ionization.

1.5.2 Detection

Upon contact with plasma, the analyte's electrons are excited and decay to ground levels. This causes the molecule to emit element specific spectra in the UV/visible region of 160 to 800 nm, which are detected and measured to determine concentration. Spectrometer mirrors then focus the emitted radiation to the entrance slit of wavelength dispersing device. These dispersing devices are usually comprised of diffraction gratings, however more recent systems use echelle gratings. The echelle grating system utilizes properties of a diffraction grating and a prism. The course grating of the echelle first separates out spectra by their wavelengths in multiple overlapping spectral orders. A second grating then disperses the spectral orders, producing a two dimensional separation (Fig. 1.4), wavelength in one direction and spectral order in another. This solid state detection system provides a highly efficient and compact means of diffraction. The spectrum is then analyzed using an integrated circuit (IC) array sensors upon which the diffraction pattern is shone upon. At certain key region in the diffraction corresponding to elemental spectra, pixel sensors are placed in order to detect light emitted from the sample. The light detected by these pixels is then used to determine peak intensity for a specific element present in the sample.

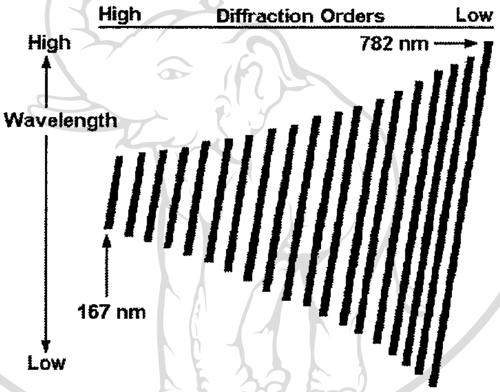

Figure 1.4 Echelle diffraction pattern showing a compact, two dimension spread[12]

1.5.3 Optimization

General operating conditions for the ICP-OES are commonly used for day to day sample analysis, resulting in accurate determination of analytes. However, due to the sensitivity of the instrument and the large number of parameters in the system, optimization can significantly improve detection. Parameters which can be modified include integration time, PMT voltage, nebulizer/argon flow rate and RF power. Integration time is the length of the time the instrument is allowed to perform analysis. Elements that are expected to have weak signals may be given longer integration time, and also allows better precision.

Nebulizer uptake rate can be varied depending on the speed at which ionization occurs within the plasma. Generally this is set to 1 ml/min but can be reduced to 0.7 ml/min for slower ionizing elements, or increased for sodium and potassium which ionize too quickly to emit radiation.

RF power determines the strength of the plasma, and is generally set at 1.3 kW or 1.4 kW for normal use of the ICP-OES. A setting higher than 1 kW is used because the plasma is more robust at these conditions, as indicated by the Mg line. Increasing the RF power decreases ionization time, especially for halides such as Br, Cl and I which have much higher ionization energies compared to other elements.

1.5.4 Effectiveness

ICP-OES is an effective instrument in measuring Ba and other low concentrations of elements in solution due to its low detection limits, and wide dynamic range.

ICP-OES has detection limits of 100 μg/l to 1 μg/l in radial mode, and 10 μg/l to 0.1 μg/l in axial mode. While these limits are moderate in comparison to GFAAS (0.1 μg/l to 0.01 pg/l) the dynamic range of the ICP is much wider, ranging from 5.5 orders of magnitude, in comparison to GFAAS (2 orders of magnitude) and FAAS (3 orders of magnitude).

Detection limits for Ba measurement using the ICP-OES is 0.03 µg/l. For rough quantitation (+/- 10%) a concentration at least 5 times that of the detection limit is suggested. For normal quantitation (+/- 2%) suggested concentration is at least 100 times the detection limit.

Unlike most atomic absorption instruments such as flame and graphite furnace, ICP-OES has multi-element capability, since the plasma ionizes all atoms in the sample and emits the spectra for each one. The instrument is capable of detecting up to 40 elements per minute, with a calibration time of only 10-35 seconds. There are, however, some elements that are not easily detected using this instrument. Argon cannot be measured using this instrument, since it is the carrier gas used during operation. Oxygen, carbon, hydrogen and nitrogen are very difficult to measure because of their abundance within the system outside of what is introduced through the sample uptake. Halides such as Br, Cl and I are measurable, but may be difficult because of their high ionization energies, however modification of technique can allow these to be analyzed. Radioactive elements and those that have short half-lives are not recommended for this technique.

1.6 Aims of research

The aims of this research work were summarized as follows:

1. To investigate the optimum conditions for the reduction of Pb(II), Cr(III), Cu(II) and Cd(II) ions in contaminated water samples using dried seaweed.

2. To investigate the optimum conditions for the reduction of Pb(II), Cr(III), Cu(II) and Cd(II) ions in contaminated water samples using the modified seaweed.

3. To apply the proposed method for the reduction of Pb(II), Cr(III), Cu(II) and Cd (II) ions in wastewater samples from two sampling areas namely the plating factory and the treatment plant.