CHAPTER 1

INTRODUCTION

At present, adsorbent material have been widely prepare processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions. These porous materials have capacity or tendency to physically chemical adsorb substances. This study has focused on producing low-cost adsorbent materials using wastes from the Mae Moh electric power plant in Lampang such as bottom ash (BA) and flue gas desulfurization (FGD) gypsum as novel adsorbent materials for dye removal in water waste.

The Mae Moh power plant in Lampang is a lignite coal fired thermal power plant. The production of power through combustion produces a huge amount of wastes. Virtually every economical use of coal is affected by the amount and variety of waste products. The types of wastes left over from burning of coal are fly ash (FA), BA, boiler slag and FGD gypsum. Wastes in coal can be the source of deleterious pollutants and corrosive elements, but also a source of useful by-products. Since 1960 many applications were identified in previous years using BA and FGD gypsum as a substitute for light fill material in construction [1], as engineering material [2], soil amendment [3], improvement of the physical properties of soil [4-6] adsorbents of heavy metals and organic substances [7-10] in previous years. However, its capability

to absorb fertilizers [11] is not much exploited so far. In the first chapter, Adsorbent materials, from plant waste, Dry types Surface area analysis is distribute as follow:

1.1 Adsorbents

Due to adsorbent materials must be amended to provide the appropriate physical and chemical properties necessary for adsorption of dyes. The following is a description of some of the most commonly used amendments for production of the adsorbent materials.

1.1.1 Powdered Activated Carbon [12]

Powdered activated carbon, or PAC, is a form of activated carbon with a very small particle size. Treatment involves adding PAC to water, allowing the PAC to interact with contaminants in the water, then removing the PAC by sedimentation or filtration. The feed location of PAC can be at any point prior to filtration. The most common locations are in the flash mixer or flocculator since these pieces of equipment will mix the PAC into the water very well. However, some plants feed PAC just before filtration so that the PAC will form a layer on top of the filter and ensure that all water comes in contact with the activated carbon. Adding PAC just before filtration can cause problems, though, since the small PAC particles can pass through the filters and cause dirty water complaints from customers or can cake filters and result in reduced filter runs.

Regardless of the feed location, PAC can be added to water using either a dry feeder or as a slurry. Dry feeders are most often used in small plants when PAC is fed at intervals in response to periodic taste and odor problems. In

contrast, slurries (mixtures of PAC with water) are used in larger plants or when PAC is fed continuously. Since it is difficult to make the PAC mix with water, the mixer should have an overhead spray system. The effectiveness of PAC in adsorbing tastes and odors depends on adequate mixing, contact time, dosage, and on the cause and concentration of the taste/odor problem. Mixing and contact time are determined by the location at which the PAC is added in the treatment process, so adjustments made by the operator will usually involve only dosage adjustments. The dosage usually ranges from 1 to 15 mg/L but must be much higher, in the range of 100 mg/L or more, when the PAC is being used to remove trihalomethanes or trihalomethane precursors. The operator chooses an appropriate dosage using jar tests and the results from odor and taste tests.

Fig 1.1 Powdered Activated Carbon

1.1.2 Granular Activated Carbon

Granular activated carbon, also known as GAC, has a larger particle size than PAC with an associated greater surface area. Like PAC, GAC can remove trihalomethane precursors as well as taste and odor compounds. GAC is used as a filter medium, either as a layer in a rapid-sand filter or in a separate filter known as a

contactor. When contactors are used, the contactor is placed downstream of the filter so that turbidity won't clog the contactor.

Like filters, contactors must be designed to provide adequate contact time of water with the filter medium. This is done by calculating the empty bed contact time, or EBCT, which is calculated similarly to detention time, as the volume of the filter divided by the flow rate. The calculation is called "empty bed contact time" because the volume taken up by the GAC in the contactor is not taken into account. Empty bed contact time should be about ten minutes.

During operation of a GAC filter or contactor, a variety of factors must be monitored. If the GAC is part of a filter designed to remove particulate matter as well as to adsorb tastes and odors, then the effluent turbidity should be monitored. Similarly, the taste and odor contaminants in the effluent should be monitored to determine whether the GAC is operating properly. The operator should make regular checks for bacteria since microorganisms often grow on GAC filters and result in clogging problems. Finally, head loss must be monitored as it would be for any other filter to determine when the unit needs to be backwashed. Washing a GAC filter involves backwashing with a 50% bed expansion and surface washing.

Although GAC filters can be operated like a rapid sand filter in most ways, backwashing and surface washing are not the only cleaning required for the units. The entire surface of the GAC will eventually become covered with contaminants, just as a softener's resin will become covered with magnesium and calcium ions. A GAC filter can typically operate for months or years before reaching this state, depending on the contaminant levels in the influent water. Once the GAC

has reached its adsorption capacity, it must be regenerated using the same heating process used to activate the carbon. In many plants, GAC is simply replaced rather than investing in the equipment required for regeneration.

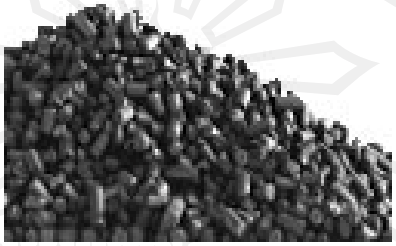


Fig 1.2 Granular activated carbon

1.1.3 Deoiled soya [13]

Granular activated carbon, also known as GAC, has a larger particle Deoiled soya a yellow color, an agricultural waste, for the adsorptive removal of dye from its aqueous solutions. as shown in Fig. 1.3. Deoiled soya was first washed with double-distilled water and dried. To remove the adhering organic impurities, dried materials was then dipped in hydrogen peroxide. Adsorbents was then washed and dried in an oven for optimum time to remove moisture. Deoiled soya was sieved to desired particle size.

Fig 1.3 Deoiled soya

1.1.4 Extruded Activated Carbon (Eac) [14]

Porous carbons containing several types of inorganic impregnant such as iodine, silver, cation such as Al, Mn, Zn, Fe, Li, Ca have also been prepared for specific application in air pollution control especially in museums and galleries. Due to antimicrobial/antiseptic properties, silver loaded activated carbon is used as an adsorbent for purifications of domestic water. Drinking water can be obtained from natural water by treating the natural water with a mixture of activated carbon and flocculating agent $Al(OH)_3$. Impregnated carbons are also used for the adsorption of H_2S and mercaptans. Adsorption rates for H_2S as high as 50% by weight have been reported.

Fig 1.4 Extruded Activated Carbon

1.1.5 Zeolites [15]

Zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents. The term zeolite was originally coined in 1756 by Swedish mineralogist Axel Fredrik Cronstedt, who observed that upon rapidly heating the material stilbite, it produced large amounts of steam from water that had been adsorbed by the material. Based on this, he called the material *zeolite*, from the Greek.

Fig 1.5 Zeolites

1.1.6 Silica gel [16]

Silica gel is a granular, vitreous, highly porous form of silica made synthetically from sodium silicate. Despite its name, silica gel is a solid. It is a naturally occurring mineral that is purified and processed into either granular or beaded form. As a desiccant, it has an average pore size of 2.4 nanometers and has a strong affinity for water molecules.

Silica gel is most commonly encountered in everyday life as beads packed in a vapor-permeable plastic. In this form, it is used as a desiccant to control local humidity in order to avoid spoilage or degradation of some goods. Because of poisonous dopants (see below) and their very high absorption of moisture, silica gel packets usually bear warnings for the user not to eat the contents. If consumed, the pure silica gel is unlikely to cause acute or chronic illness. Food-grade desiccant should not include any poisons which would cause long-term harm to humans if consumed in the quantities normally included with the items of food.

Fig 1.6 Silica gel

1.2 Power plant wastes

1.2.1 Fly ash [17]

Fly ash is one of the residues generated in combustion, and comprises the fine particles that rise with the flue gases. Ash which does not rise is termed bottom ash. In an industrial context, fly ash usually refers to ash produced during combustion of coal. Fly ash is generally captured from the chimneys of coal-fired power plants, and together with bottom ash removed from the bottom of the furnace is in this case jointly known as coal ash. Depending upon the source and make-up of the coal being burned, the components of fly ash vary considerably, but all fly ash includes substantial amounts of silicon dioxide (SiO_2) (both amorphous and crystalline) and calcium oxide (CaO), both being endemic ingredients in many coal-bearing rock strata.

Toxic constituents depend upon the specific coal bed make-up, but may include one or more of the following elements or substances in quantities from trace amounts to several percent: arsenic(As), beryllium(Be), boron(B), cadmium(Cd),

chromium(Cr), chromium VI(Cr-51), cobalt(Co), lead(Pd), manganese(Mn), mercury(Hg), molybdenum(Mo), selenium(Se), strontium(Sr), thallium(TI), and vanadium(V), along with dioxins and PAH compounds.

In the past, fly ash was generally released into the atmosphere, but pollution control equipment mandated in recent decades now requires that it be captured prior to release. In the US, fly ash is generally stored at coal power plants or placed in landfills. About 43 percent is recycled, often used to supplement Portland cement in concrete production. Some have expressed health concerns about this.

In some cases, such as the burning of solid waste to create electricity ("resource recovery" facilities a.k.a. waste-to-energy facilities), the fly ash may contain higher levels of contaminants than the bottom ash and mixing the fly and bottom ash together brings the proportional levels of contaminants within the range to derive as nonhazardous waste in a given state, whereas, unmixed, the fly ash would be within the range to signify as hazardous waste.

Fig 1.7 Fly ash

1.2.2 Bottom ash [18-20]

Bottom ash is made from agglomerated ash particles that are too large to be carried in the flue gases and fall through open grates to an ash hopper at the bottom of the furnace. Bottom ash, a dark gray, porous, granular material sand size is able to use as a low cost replacement for more expensive sand in ceramic industry. Many elements in bottom ash such as calcium(Ca), iron(Fe), potassium(K) and magmesium(Mg) are essential for plant nutrient.

Fig 1.8 Bottom ash

1.2.3 Flue gas desulfurization gypsum [18-20]

Considerable amounts of FGD gypsum are generated when sulfur is recovered from coal burning at electrical generating plants to meet Clean Air standards. FGD gypsum is the solid material resulting from the removal of sulfur dioxide gas from the utility boiler stack gases in the flue gas desulfurization process. The material is produced in the flue gas scrubbers by reacting slurred limestone or lime with the gaseous sulfur dioxide to produce calcium sulfite. Some utility plants further oxidize the calcium sulfite to calcium sulfate (which is the same as natural gypsum). FGD gypsum is 95% pure calcium sulfate and has found to have many

applications. Gypsum has the ability to improve the physical properties of soil such as water infiltration, increased electrolyte concentration of water at the surface of the soil causing soil flocculation thus reducing sealing, help alleviate soil compaction and improved aggregate stability of soils.

Fig 1.9 FGD gypsum

1.3 Dye Types [21]

The first human-made (synthetic) organic dye, mauveine, was discovered by William Henry Perkin in 1856. Many thousands of synthetic dyes have since been prepared. Synthetic dyes quickly replaced the traditional natural dyes. They cost less, they offered a vast range of new colors, and they imparted better properties to the dyed materials. Dyes are now classified according to how they are used in the dyeing process.

1.3.1 Acid dyes [21]

Acid dyes are water-soluble anionic dyes that are applied to fibers such as silk, wool, nylon and modified acrylic fibers using neutral to acid dye baths.

Attachment to the fiber is attributed, at least partly, to salt formation between anionic groups in the dyes and cationic groups in the fiber. Acid dyes are not substantive to cellulosic fibers. Most synthetic food colors fall in this category.

Methyl orange belongs to the azodyes. It is prepared by coupling diazotized sulphanilic acid with dimethylaniline [22].

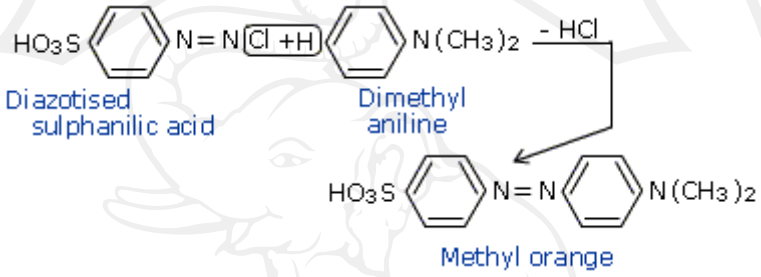


Fig 1.10 Production of methyl orange

This acid dye is used for wool and silk. It imparts an orange color, as the name suggests though the color is not fast to light or wash.

1.3.2 Basic dyes [21]

Basic dyes are water-soluble cationic dyes that are mainly applied to acrylic fibers, but find some use for wool and silk. Usually acetic acid is added to the dyebath to help the uptake of the dye onto the fiber. Basic dyes are also used in the coloration of paper.

1.3.3 Direct or substantive dyeing [21]

Direct or substantive dyeing is normally carried out in a neutral or slightly alkaline dyebath, at or near boiling point, with the addition of either sodium

chloride (NaCl) or sodium sulfate (Na_2SO_4). Direct dyes are used on cotton, paper, leather, wool, silk and nylon. They are also used as pH indicators and as biological stains.

1.3.4 Mordant dyes [21]

Mordant dyes improve the fastness of the dye against water, light and perspiration. The choice of mordant is very important as different mordants can change the final color significantly. Most natural dyes are mordant dyes and there is therefore a large literature base describing dyeing techniques. The most important mordant dyes are the synthetic mordant dyes, or chrome dyes, used for wool; these comprise some 30% of dyes used for wool, and are especially useful for black and navy shades. The mordant, potassium dichromate, is applied as an after-treatment. It is important to note that many mordants, particularly those in the heavy metal category, can be hazardous to health and extreme care must be taken in using them.

1.3.5 Vat dyes [21]

Vat dyes are essentially insoluble in water and incapable of dyeing fibers directly. However, reduction in alkaline liquor produces the water soluble alkali metal salt of the dye, which, in this leuco form, has an affinity for the textile fiber. Subsequent oxidation reforms the original insoluble dye. The color of denim is due to indigo, the original vat dye.

1.3.6 Reactive dyes [21]

Reactive dyes utilize a chromophore attached to a substituent that is capable of directly reacting with the fiber substrate. The covalent bonds that attach

reactive dye to natural fibers make them among the most permanent of dyes. "Cold" reactive dyes, such as Procion MX, Cibacron F, and Drimarene K, are very easy to use because the dye can be applied at room temperature. Reactive dyes are by far the best choice for dyeing cotton and other cellulose fibers at home or in the art studio.

1.3.7 Disperse dyes [21]

Disperse dyes were originally developed for the dyeing of cellulose acetate, and are water insoluble. The dyes are finely ground in the presence of a dispersing agent and sold as a paste, or spray-dried and sold as a powder. Their main use is to dye polyester but they can also be used to dye nylon, cellulose triacetate, and acrylic fibers. In some cases, a dyeing temperature of 130 °C is required, and a pressurised dyebath is used. The very fine particle size gives a large surface area that aids dissolution to allow uptake by the fiber. The dyeing rate can be significantly influenced by the choice of dispersing agent used during the grinding.

1.3.8 Azo dyes [21]

Azoic dyeing is a technique in which an insoluble azo dye is produced directly onto or within the fiber. This is achieved by treating a fiber with both diazoic and coupling components. With suitable adjustment of dyebath conditions the two components react to produce the required insoluble azo dye. This technique of dyeing is unique, in that the final color is controlled by the choice of the diazoic and coupling components.

1.3.9 Sulfur dyes [21]

Sulfur dyes are two part "developed" dyes used to dye cotton with dark colors. The initial bath imparts a yellow or pale chartreuse color, This is after treated with a sulfur compound in place to produce the dark black we are familiar with in socks for instance. Sulfur Black 1 is the largest selling dye by volume.

1.4 Test procedure for physical and chemical analysis

1.4.1 The pH value [23]

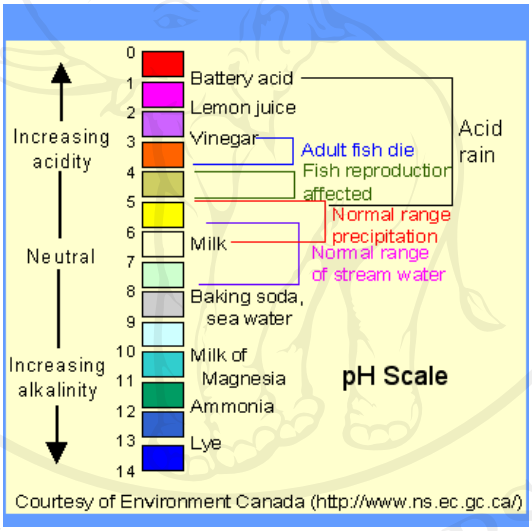


Fig 1.11 The pH scale

Acidic and basic are two extremes that describe a chemical property of chemicals. The pH scale measures how acidic or basic a substance is. The pH scale ranges from 0 to 14. A pH of 7 is neutral. A pH less than 7 is acidic. A pH greater than 7 is basic. (Fig. 1.9). Monitoring the pH can ensure that the adsorbent material have the optimum pH for adsorption.

1.4.2 Surface area [24]

Adsorption of a gas on a solid surface may happen physically or chemically, depending on the materials in the temperature. For surface area determinations, physical adsorption is desirable. Since chemisorption involves activation energy, this is usual to be carried out at very low temperature to ensure only physical adsorption, and to use a relatively inert gas such as nitrogen. Hence, adsorption of nitrogen, at liquid nitrogen temperature, is a common technique. The theory of Brunauer, Emmett and Teller (BET) method is widely used in surface science for the calculation of surface areas of solids by physical adsorption of gas molecules. A total surface area (S_{total}) and a specific surface area (S) are evaluated by the following equations (1.1) and (1.2).

$$S_{total}/w = V_m Ns/MW \qquad (1.1)$$

$$S = S_{total}/MW \qquad (1.2)$$

where N = Avogadro's number, s = cross section of adsorbate, MW = molecular weight of adsorbate, w = weight of sample solid, and V_m = the monolayer adsorbed gas quantity.

1.4.3 Density and water absorption [25]

The density of a material has been defined as the relationship between its mass (weight) and its volume;

$$\text{Density} = (\text{mass/volume}) \qquad (1.3)$$

The water absorption was calculated according to:

$$\text{Water absorption (WA)} = \frac{m_2 - m_1}{m_1} \times 100\ (\%) \qquad (1.4)$$

or

$$\text{WA \%} = \{(S-D)/D\}100 \qquad (1.5)$$

where m_1 is the dry mass (g) and m_2 soaked mass (g).

1.4.4 X-ray fluorescence spectrometry [26-27]

The main principle of X-ray fluorescence (XRF) spectrometry is that X-rays of characteristic wavelength (and energy) are emitted from a sample when the sample is ionized by a stream of X-rays. The use of XRF technique for the analysis of minerals has gained since the specification of commercially available equipment has vastly improved. For normal analytical purposes the instrument is set up to determine: 1) the common elements (silicon (Si), aluminum (Al), iron (Fe), titanium (Ti), calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K)) found in most ceramic materials. 2) the trace elements (manganese (Mn), chromium (Cr), phosphorous (P), zirconium (Zr), hafnium (Hf), barium (Ba) and tungsten (W)). Principles: The XRF principle is depicted in Fig. 1.11. An inner shell electron is excited by an incident photon in the X-ray region. During the de-excitation process, an electron is moving from a higher energy level to fill the vacancy. The energy difference between the two shells appears as an X-ray, emitted by the atom. The X-ray spectrum acquired during the above process reveals a number of characteristic peaks. The energy of the peaks leads to the identification of the elements present in the sample (qualitative analysis), while the peak intensity provides the relevant or

absolute elemental concentration (semi-quantitative or quantitative analysis). Atypical XRF spectroscopic arrangement (Fig. 1.10) includes a source of primary radiation (usually a radioisotope or an X-ray tube) and an equipment for detecting the secondary X-rays.

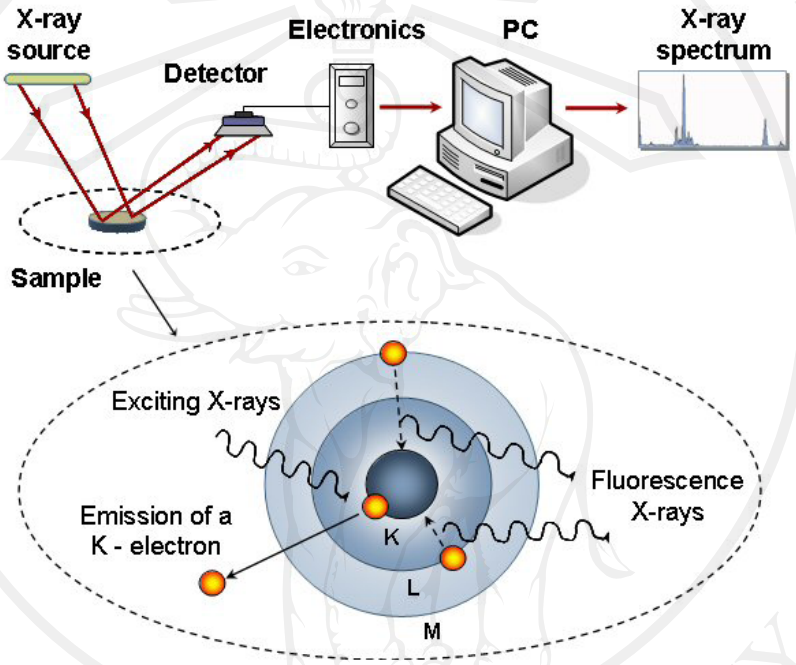


Fig 1.12 Schematic diagram of XRF and the typical XRF detection arrangement.

The instrumentation consists of a source for primary X-rays, collimators, analyzing crystal and detector. Applications: It is one of the non-destructive methods in the elemental analysis of solid or liquid samples for major and minor constituents. Most of the elements in the periodic table, both metals and nonmetals, respond to this technique. Detection limit is between 10 to 100 mg/L.

Disadvantages: The sensitivity is affected for elements with lower atomic numbers, particularly elements with atomic number lower than 15 are difficult

to analyze. The sensitivity is also limited by matrix absorption, secondary fluorescence and scattering of the particles. Instruments are often large, complicated and costly.

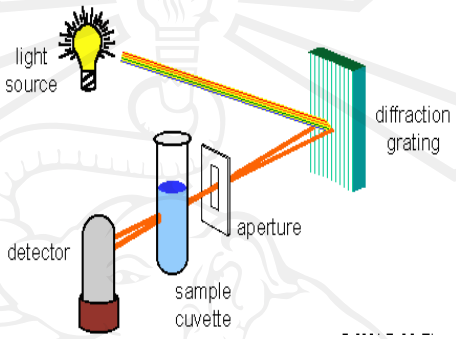
1.4.5 Ultraviolet - visible spectroscopy [28]

Principles: It involves the absorption of electromagnetic radiation by the substances in the visible and ultraviolet regions of the spectrum. This will result in changes in the electronic structure of ions and molecules.

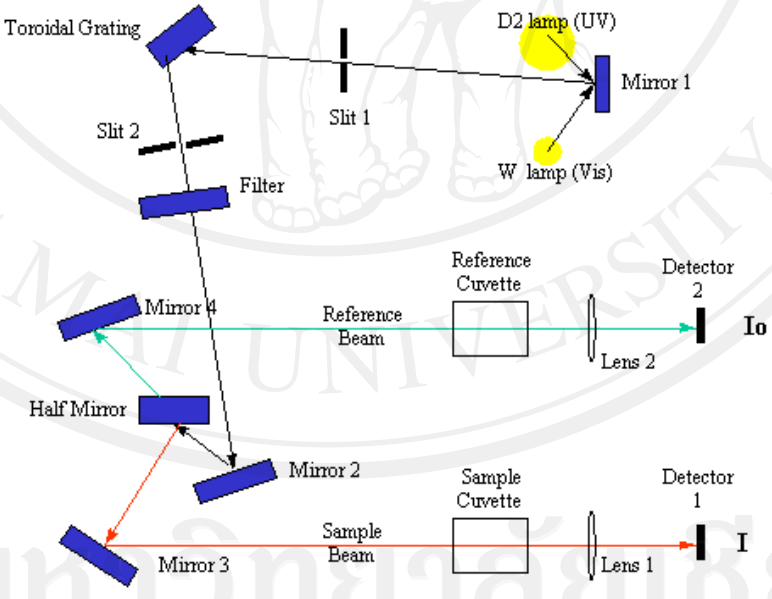
Instrumentation: It consists of a dual light source (tungsten lamp for visual range measurements and deuterium lamp for measurements at ultra-violet regions), a grating monochromator, photo detector, mirrors and glass or quartz cells. For measurements to be made under visible region, both glass and quartz cells can be used. For the measurements under ultra-violet region, only quartz cell should be used, since, glass cells absorb ultra-violet rays. There are two types of instruments for this technique as single beam and double beam spectrophotometers. However, nowadays, double beam spectrophotometers are widely used.

Applications: It is the most widely used technique for quantitative trace analysis, for the Beer-Lambert law is applied. Sometimes it is used in conjunction with other techniques in the identification and structural analysis of organic materials. For qualitative analysis the so-called “molecular absorption spectrum” is obtained, which exactly tells the nature of the compound-since no two compounds can have the same absorption and hence the same spectrum.

Disadvantages: Samples should be in solution. Mixture of substances poses difficulties to analyse and requires prior separation. Interference sometime makes the measurement difficult, but these disturbances are quite common with these types of techniques.



(a)



(b)

Fig 1.13 Schematic diagram of UV-Vis spectrophotometer : (a) singer beam and (b) double beam spectrophotometers

1.5 Absorption and adsorption [29]

Sorption reactions generally occur over a short period of time, however if the adsorbed contaminant begins to be incorporated into the structure of the sorbent, a slow occurring reaction, known as absorption, begins to take place. To be more precise, the difference between adsorption and absorption is that adsorption is the attraction between the outer surface of a solid particle and a contaminant, whereas absorption is the uptake of the contaminant into the physical structure of the solid. Fig 1.14 shows the primary differences between intraparticle absorption versus surface adsorption. The main difference is that some contaminant particles are attracted to the outer surface of the soil particle, while another has been actually incorporated into the particle's structure.

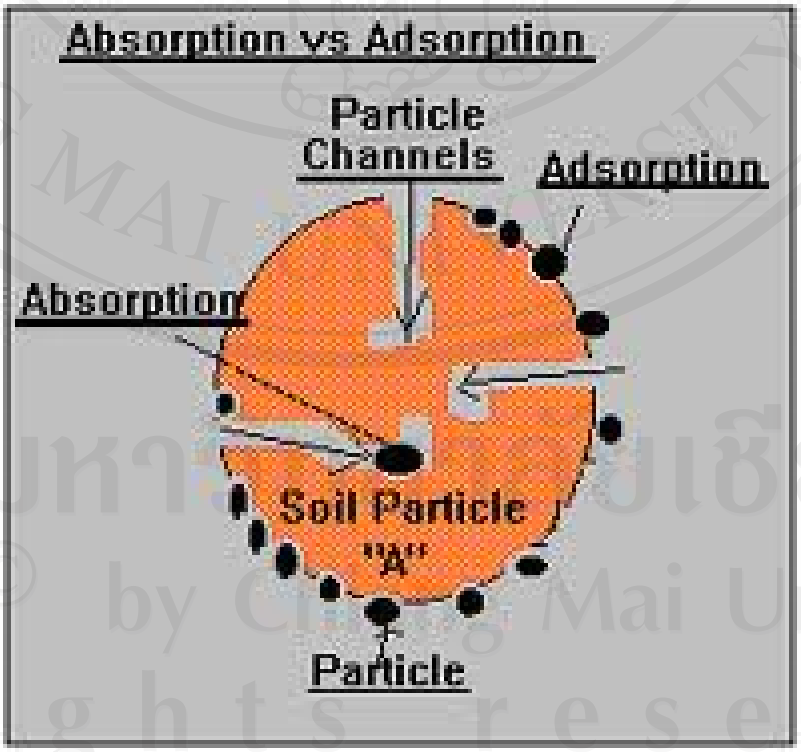


Fig 1.14 Absorption and adsorption[29]

Adsorption is a term used to describe the process by which material accumulates at the interface between two phases. These phases can be liquid-liquid, liquid-solid, gas-liquid, and gas-solid. In this process, the adsorbing phase is termed adsorbent, whereas the substance being adsorbed is called adsorbate. Adsorption can be applied in both gaseous and liquid separations. Adsorption of a material occurs at the surface since it reduces the imbalance of attractive forces, and, therefore, the surface free energy of the heterogeneous system. The adsorption using the batch-type techniques is expressed in the form of equilibrium concentration, C_e, versus adsorbed concentration, q_e, of the solute. The adsorbed amount, q_e, was calculated using the following equation (1.6):

$$q_e = \{(C_0-C_e)V_e\}/ W \qquad (1.6)$$

where C_0 = initial concentration of the solute (mg/L), C_e = equilibrium concentration or final concentration of the solute (mg/L), V = volume of solution (mL) and W = mass of adsorbent materials expressed on an oven-dried basis (g).

1.5.1 Physical adsorption and chemical adsorption [30]

Adsorption is divided into the two sub-categories of physical adsorption (physisorption) or van der Waals adsorption and chemical adsorption (chemisorption). The adsorption process can be determined whether chemical bonds are formed during the process. Physisorption is applicable to all adsorbate-adsorbent systems under the suitable conditions of pressure and temperature whereas chemisorption may only occur if the system is capable of making a chemical bond.

1.5.1.1 Physical adsorption

The process is a dynamic one where an equilibrium state exists with molecules and the interaction between the adsorbate and adsorbent. No chemical bonds are formed during physical adsorption; attraction between the adsorbate and adsorbent exists by the formation of intermolecular electrostatic, such as London dispersion forces, or van der Waals forces from induced dipole-dipole interactions, or may be dependent on the physical configuration of the adsorbent such as the porosity of activated carbons. Dispersion forces are the result of rapid fluctuations in the electronic density of one adsorbent molecule inducing an electrical moment in a second atom. If the adsorbate possesses a permanent dipole, or even a multipole, then additional interactions may occur, as charge distributions are induced in the adsorbent and interactions of these moments with any permanent field of the solid. The process is a very general one and is analogous with that of condensation. Physisorption occurs to varying extents for all adsorbates, gases and vapors, with all adsorbing solids and the effect increases with decreasing temperature or increasing pressure. Physical adsorption is based on certain basic considerations and adsorption on a heterogeneous surface, that is a surface on which the sites are different, occurs at the sites of highest adsorption potential. The process of physical adsorption into the microporous structure of activated carbon follows the theory of Dubinin. The mechanism of adsorption is dependent upon the size of the admolecule in comparison with the pore width due to the energetic interactions between the chosen adsorbate and the pores. Admolecules initially adsorb into the pores with the highest energy, ignoring activated diffusion effects, then adsorption proceeds via filling of progressively larger, or decreasing energy, porosity. Some pores are capable of accommodating two or three

surfaces that physical adsorption is independent of the surface chemistry of the adsorbent.

1.5.1.2 Chemical adsorption

Chemisorption involves the transfer of electrons between the adsorbent and the adsorbate with the formation of chemical bonds, by chemical reaction, between the two species causing adhesion of the adsorbate molecules. Chemical adsorption is far less common than physical adsorption and due to the chemical bonds formed regeneration of the adsorbent for subsequent re-use is often difficult or impossible. Due to the fact that chemical bonds are formed during the adsorption process, desorption of the adsorbed phase may yield products which are chemically different to the original adsorbate.

1.5.2 Classification of adsorption isotherm

Adsorption isotherms should conventionally be plotted on the basis of relative pressure, (x-axis) versus amount adsorbed expressed as a molar quantity (y-axis) in mmol g^{-1}, to allow comparisons to be made. The six IUPAC standard adsorption isotherms are shown in Fig. 1.15 because the systems demonstrate different gas/solid interactions.

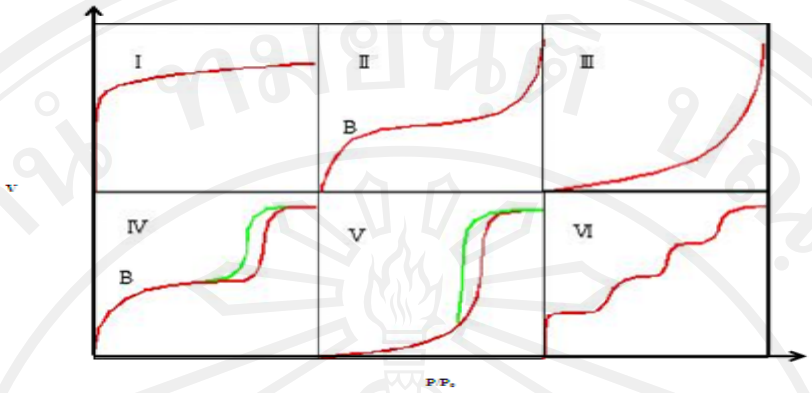


Fig 1.15 Six types of adsorption isotherms

The Type I isotherm is typical of monolayer adsorption. This type of curve is obtained by low temperature adsorption. The chemisorption phenomena frequently produce this curve. Type II is the most frequently encountered adsorption isotherm and is referred to as the sigmoid or S-shape isotherm. The first portion of the curve up to relative pressure corresponds to monolayer. This is followed by a multilayer region. Type III and type IV are typical of vapor adsorption (i.e. water vapor on hydrophobic materials). Type V and V feature a hysteresis loop generated by the capillary condensation of the adsorbate in the mesopores of the solid. Finally, the rare type VI step-like isotherm is shown by gas adsorbed on special adsorbent.

1.5.3 Isotherm equations

1.5.3.1 Langmuir isotherm

The adsorption equation was developed by Langmuir in 1916. Langmuir equation was one of the first and most important equations based on theory. In the assumptions of Langmuir isotherm, the energy of adsorption is constant, and

the number of binding sites is finite. The equation for the Langmuir isotherm is shown here:

$$q_e = q_{max}bC_e/1+bC_e \quad (1.7)$$

where q_{max} = saturation limit and b = a temperature dependent equilibrium constant. The constant q_{max} corresponds to the surface concentration at monolayer coverage and represents the maximum value of q_e that can be achieved as the equilibrium concentration C_e is increased. The constant b is related to the energy of adsorption and increases as the strength of the adsorption bond increases. In order to evaluate the Langmuir constants, a linear form of the Langmuir equation is used:

$$C_e/q_e = 1/bq_{max} + C_e/q_{max} \quad (1.8)$$

A plot of C_e/q_e versus C_e will yield a straight line for data which fits the Langmuir expression. Hence, from the gradient, $1/q_{max}$, and intercept, $1/bq_{max}$, the Langmuir constants can be calculated.

1.5.3.2 Freundlich isotherm

This isotherm is an empirical expression and has no physical basis, hence the equilibrium relationship proposed by Freundlich is only valid when the adsorption is a physical process without any change in the configuration of the

molecules in the adsorbed state. The equilibrium of this model is as follows in equation (1.9).

$$q_e = K_F * C_e^{1/n} \quad (1.9)$$

where q_e = equilibrium adsorbed amount on the adsorbent, C_e = equilibrium concentration, K_F and n = empirical constants depending on the nature of adsorbent and adsorbate. The constant K_F is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption, i.e. the mechanism of adsorption. The constants can be obtained by line arising in equation (1.10).

$$\log q_e = \log K_F + 1/n \log C_e \quad (1.10)$$

1.6 Research Objectives

BA and FGD gypsum used on land cause no environmental problems if these products are used appropriately. Based on these characterizations and detail studies, BA and FGD gypsum can be used as low cost substrates in the production of adsorbent material. In this study, they are mixed with paddy clay (PC), to which a small amount of sawdust was added. PC fired gained plasticity and strength with rather higher cation exchange capacity value after firing. Moreover, soil particles have a charge on their surface. The total charge on the soil is a function of both the surface area and the chemical nature of the particles. While soils have both positive and negative charges, negative surface charges usually exceed by far the positive surface

charges. Firing sawdust can be used to improve the pores in materials and to provide increased porosity. Therefore, the main objectives of this research are as follows:

1.6.1 To produce adsorbent materials using BA and FGD gypsum mixed with paddy clay and saw dust**.**

1.6.2 To study physical and chemical properties of the produced adsorbent materials.

1.6.3 To study adsorption of methyl orange and iodine on the produced adsorbent materials.