AGRICUTURAL-BASED ADSORBENTS FOR METHYLENE BLUE ADSORPTION: EQUILIBRIUM, KINETIC AND THERMODYNAMICS STUDIES

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By

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LIST OF SYMBOLS

Symbol	Description	Unit
A	Arrhenius factor	-
C_e	Equilibrium liquid phase concentration	(mg/L)
C_o	The highest initial liquid phase concentration	(mg/L)
C_t	Initial liquid phase concentration at time, t	(mg/L)
K_F	Freundlich isotherm constant	$(mg/g)(L/mg)^{1/n}$
Q_o	Langmuir isotherm constant	(mg/g)
R^2	Correlation coefficient	-
n	Freundlich isotherm constant related to adsorption intensity	-
A	Tempkin isotherm constant related to equilibrium binding energy	(l/g)
B	Tempkin isotherm constant related to heat of adsorption	-
T	Absolute temperature	K
t	Time	h or min
R	Gas constant = 8.314	J/(mol K)
R_L	Dimensionless separation factor	-
q_t	Amount of adsorption at time	(mg/g)
q_e	Equilibrium solid phase adsorbate concentration	(mg/g)
q_{max}	The maximum surface coverage of adsorbent	(mg/g)
k_1	Rate constant of first-order adsorption	(1/min)
k_2	Rate constant of second-order adsorption	(g/mg.min)
h	Initial sorption rate	(mg/g.min)
E_a	Arrhenius activation energy	(kJ/mol)
ΔG^o	Free energy Gibbs	(kJ/mol)
ΔH^o	Enthalpy	(kJ/mol)
ΔS^o	Entropy	(J/mol)
K_{id}	Intra-particular diffusion rate constant	$(mg/h^{1/2}g)$
V	Volume of solution	L
W	The weight of adsorbate	g
λ	Wavelength	nm

LIST OF ABBREVIATIONS

International Union of Pure and Applied Chemistry	IUPAC
Rotation per minute	rpm
Durian peels	DP
Banana leaves	BL
Pineapple stem	PPS
Pineapple leaves	PPL
Papaya stem	PYS
Papaya leaves	PYL

PENJERAP BERASASKAN PERTANIAN UNTUK PENJERAPAN METILENA BIRU: KAJIAN KESEIMBANGAN, KINETIK DAN TERMODINAMIK

ABSTRAK

Kajian ini tertumpu kepada penyingkiran pencelup kationik (metilena biru) dari larutan akueus dengan menggunakan sisa pembuangan pertanian sebagai penjerap. Tujuan utama kajian ini ialah untuk mengkaji penjerapan metilena biru (MB) menggunakan kulit durian (DP), daun pisang (BL), batang nenas (PPS), daun nenas (PPL), batang betik (PYS) dan daun betik (PYL). Eksperimen dijalankan secara kelompok terhadap pengaruh keadaan operasi seperti kepekatan awal (50-500 mg/L), masa sentuhan, kesan pH (2-10) dan suhu (30-50 ^{o}C). Data keseimbangan bagi penjerapan pencelup MB ke atas semua bahan penjerap telah dianalisa menggunakan model-model garis sesuhu Langmuir, Freundlich dan Tempkin. Model garis sesuhu Langmuir didapati mampu meramalkan data eksperimen dengan baik bagi semua penjerap. Tertib-pseudo-pertama, Tertib-pseudo-kedua dan model peresapan intrapartikel telah diuji dalam penyelidikan mekanisme penjerapan. Model pseudo-tertib-kedua didapati mampu meramalkan data eksperimen dengan baik bagi penjerapan pencelup MB ke atas semua penjerap ($R^2 \geq 0.964$). Nilai tenaga pengaktifan yang berada dalam julat 1.25-29.93 kJ/mol mengesahkan fenomena jerapan fizikal bagi pencelup MB ke atas semua penjerap kecuali batang betik dengan nilai tenaga pengaktifan 65.25 kJ/mol. Penjerapan MB terhadap batang nenas, daun nenas, batang betik dan daun betik adalah eksotermik manakala bagi kulit durian and daun pisang adalah proses endotermik. Penjerap yang digunakan boleh digunakan sebagai bahan penjerap berkos rendah untuk mengantikan karbon teraktif komersil.

AGRICUTURAL-BASED ADSORBENTS FOR METHYLENE BLUE ADSORPTION: EQUILIBRIUM, KINETIC AND THERMODYNAMICS STUDIES

ABSTRACT

This study focuses on the removal of cationic dye (methylene blue) from aqueous solution using agricultural waste as alternative adsorbents. The main aim of this study was to investigate the adsorption of methylene blue (MB) onto durian peel (DP), banana leaves (BL), pineapple stem (PPS), pineapple leaves (PPL), papaya stem (PYS) and papaya leaves (PYL). The effects of operating conditions such as initial dye concentration (50-500 mg/L), contact time, pH (2-10) effect, and temperature (30-50 ^{o}C) on adsorption of MB were studied in batch process. Equilibrium data for the adsorption of MB on all the adsorbents were analyzed by the Langmuir, Freundlich and Tempkin isotherm models. It was found that Langmuir isotherm model fits the data very well for all the adsorbents. Pseudo-first-order, pseudo-second-order and intraparticle diffusion were tested to investigate the adsorption mechanism. The pseudo-second-order kinetic model described the experimental data of MB dye adsorption onto all the adsorbents very well ($R^2 \geq 0.964$). The values of activation energy were in the range of 1.25-29.93 kJ/mol which confirms the physisorption nature of MB onto all the adsorbents, except for papaya stem when the activation energy was 65.25 kJ/mol. The adsorption of MB onto pineapple stem, pineapple leaves, papaya stem and papaya leaves was exothermic while on durian peels and banana leaves the adsorption process was endothermic. The adsorbents could be employed as alternatives to replace commercial activated carbon.

Chapter One
Introduction

1.1.1 Wastewater pollution and scenario in Malaysia

At the present there are more than 100,000 commercial dyes with a rough estimated global production of $7x10^5$-$1x10^6$ tons per year (Christie, 2007; Hunger, 2003). Of such a huge production the exact data on the quantity of dyes discharge in environment is not available. During coloring process, these industries generate substantial quantities of wastewater containing large amounts of dissolved dyestuffs and other products, such as dispersing agents, dye bath carriers, salts, emulsifiers, leveling agents and heavy metals (Sourja et al., 2005). Dyes and pigments represent one of the problematic groups which can be classified as anionic (direct, acid and reactive dyes), cationic (basic dyes) and non-ionic (disperse dyes) (Mall et al., 2006). Methylene blue dye has been identified as a scheduled waste under the Malaysian Environment Quality (Scheduled Wastes) regulations 1989 and thus must be disposed accordingly (Environmental Quality Act, 2001).

However, it is reported that 10-15% of the used dyes enter the environmental through wastes (Hussain, 2006; Hai et al., 2007). It is estimated that from 1 to 15% of the dye is lost during dyeing section of a textile industry process and is released in wastewaters. The big consumers of dyes are textile, dyeing, pulp and paper, tannery and paint industries, and hence the effluents of these industries as well as those from plants manufacturing dyes tend to produce wastewater contain dyes. Dyes are considered an objectionable type of pollutant because they are considered toxic (Bae and Freeman, 2007; Christie, 2007). This polluted wastewater gives negative effect on human such as skin and eye irritation, and skin sensitization leading to problems like skin irritation and also due to carcinogenicity (Rai et al., 2005; Hatch and Maibach, 1999).

The release of colored wastewater in the ecosystem is a dramatic source of a esthetic pollution, of eutrophication and of perturbations in the aquatic life. Colored wastes in the receiving streams interfere with transmission of sunlight into streams and, therefore, reduce photosynthetic activity (Namasivayam et al., 2001). They may also be toxic to some aquatic life because they contain metals, chlorides and so on. Over 90% of some 4000 dyes tested in an ETAD (Ecological and toxicological association of dyestuff) survey had LD50 values greater than 200 mg/kg. Dyes even in very low concentration affect the aquatic life and food chain (Gupta et al., 2006). Thus, the removal of dyes from colored effluents, particularly from textile industries, is one of the major environmental concerns these days.

There are a number of approaches that have been reported to remove the contaminants such as methylene blue from wastewater. Commonly used methods are physical methods such as adsorption, filtration and reverse osmosis to chemical treatment like coagulating/flocculation (Shi et al., 2007; Zhou et al., 2008), oxidation and ion ex-change. Biological methods such as aerobic and anaerobic treatment are used for the same purpose (Slokar and Marechal, 1998). Among several chemical and physical methods, adsorption is one of the effective techniques that have been successfully employed for dyes removal from wastewater (Juang et al., 2002).

1.2 Adsorption process

An adsorption process produces an effluent that is free of harmful substances such as carcinogenic aromatic amines which are produced by microbial degradation or by photo degradation using ultra violet light. Removal of dyes from wastewater using adsorption on commercial activated carbons is a very effective process, but the high cost of such adsorbent has motivated the search for alternatives and low-cost adsorbents (Crini., 2006). Recently many researchers attempted to use alternative low-cost adsorbents to substitute the more expensive, commercially available activated carbons. Such alternatives include biosorbents, natural materials and agricultural wastes and industry by-products. An extensive list of sorbent literature for dye removal has been compiled recently by Gupta and Suhas (2009). Since cost is an important parameter in most developing countries, efforts have been made to explore the possibility of using various low cost adsorbents.

1.3 Biomass

Biomass is term of all organic material from plants; either land or water based vegetation, as well as organic wastes (Mckendry, 2002). Biomass such as durian peel, pineapple leaves and stems, papaya leaves and stems and banana leaves has been a waste biomass for a long time. In Asian countries, particularly Malaysia, biomass generation is significantly high due to weather, and fertility and sosio-economic factors.

The abundance of biomass is allowed to rot and worse is openly burnt. Both actions affect environmental health and safety. Open burning promotes green house effect due to excessive release of carbon monoxide and carbon dioxide gasses.

In this research, low value agricultural by-products are used as adsorbents. It will help to solve part of the problem of wastewater treatment in Malaysia. The by-products include soft lignocellulosics such as pineapple stems, pineapple leaves, papaya stems, papaya leaves and banana leaves and harder material such as durian peel.

1.4 Adsorbents

In the literature, the most important desirable properties of the adsorbent are low-cost and abundant, large active surface area and containing active functional groups such as amino, hydroxyl, carboxyl, sulfate, phosphate. In this case as the agro-materials obtained from durian peel, banana plant, pineapple plant and papaya plant are abundant waste in Malaysia and also because it also mainly composed of cellulose, hemicelluloses and lignin, they can be considered as a good sorbent for this application (Demir et al., 2008). In this work, durian peel, pineapple stems, pineapple leaves, papaya stems, papaya leaves and banana leaves are used as adsorbent to remove methylene blue dye from aqueous solution.

1.4.1 Durian peel

Durian (*Durio zibethinus* Murray) a tropical fruit, is one of the planted fruit crops in Malaysia. It belongs to the genus *Durio*, which is a member of the family Bombacaceae and consists of 28 species (Brown MJ. Durio, 1997; Subhadrabandhu and Ketsa, 2001). Only one third of durian is edible, whereas the seeds (20-25%) and the shells are usually thrown away. Due to wide consumption of durians, there are lots of peels disposed as waste, causing severe problem to the community. In the interest of the environment, attempts have recently been made to use this agricultural waste as a source of valuable materials with commercial importance, for example, Khedari and colleagues (2003) used durian rinds to develop a new particleboard as a component of construction panels for energy conservation in building. Previous studies dedicated by Pongsamart and co-workers (1998) have isolated the water-insoluble and water-soluble polysaccharides from the rind, which have found potential as pharmaceutical percipients. Their applications such as a table binder, tablet disintegrator and gelling agent have been well reported (Pongsamart and

Panmaung, 1998; Umprayn et al., 1990). Chandra et al., (2007) prepared activated carbon from durian shell.

1.4.2 Pineapple stems and leaves

The pineapple (*Ananas comosus* Merr.) is the leading edible member of the family Bromeliaceae. Pineapple is cultivated in tropical countries, such as China, India, Thailand, Indonesia, Taiwan and Malaysia. According to the FAO online databases, those countries are the leading producers of pineapple in 2003 Malaysia is around 255,000 T. Pineapple is mainly produced as canned fruits and consumed worldwide. Normally leaves on farmland are used as a natural compost material or burned on site after the harvest, creating a point source of air pollution. The remaining outer peel (skin) and core from the canning are called the pineapple bran which, in turn, is a good feed for ruminants. The major constituents of pineapple leaf are cellulose (70-80 %), lignin (5-12 %) and hemicellulose (Saha et al., 1991). However, some studies have focused on improving the use of this natural bio-adsorbent in short and fiber-reinforced rubber composites (Monanty et al., 2000; Lopattananon et al., 2006). On the other hand, the crown leaves are the burden of the canned pineapple industry because the need of these leaves for replanting is relatively small compared to the amount of the refuse generated (Ai Tan et. 2001). Pineapple stems and leaves which are generated as waste in pineapple plantation and have otherwise no commercial worth are better used as alternative adsorbent in this work.

1.4.3 Papaya stems and leaves

The papaya is the fruit of the tree *Carina papaya*, in the genus *Carica*. It is native to the tropics of the America and was cultivated in Mexico for several centuries. Papaya is a short-lived, fast growing; woody, grows 10 or 12 feet in height. However, the papaya tree is chopped down after several times of harvesting. The trunks, leaves and foliage of the papaya tree are thrown away. Reutilization of papaya wastes is useful. Following work relates to adsorption in properties of papaya plantations and has otherwise no commercial worth. Asma et al., (2007) has explored the potential of papaya wood waste to treat wastewaters contaminated with heavy metals. Other than this study, a unique adsorption was developed by penetrating fungal hyphea in structural fibrous network of papaya wood (SFNPW) and successfully used for the removal of Zn(ll) from aqueous solution. Application of this new immobilization of *Phanerochaete chrysosporium* onto SFNPW, for the production of biosorbent system to remove Zn(ll), illustrating its application potential for the treatments of wastewaters containing heavy metals (Iqbal and Saeed, 2006). Iqbal and co-worker continued research to enhance the metal removing capacity of fungus adsorbent with a new idea of producing a hybrid biosorbent (HB) matrix by combining two different biosorbents using simple and low-cost immobilization technique for the sorption of Cd (ll) (Iqbal et al., 2007).

1.4.4 Banana leaves

Banana (*Musa sapientum*) is a common name for herbaceous plants of the genus *Musa*, and is also the name given to fruit of these plants. They are native to the tropical region of Southeast Asia and Australia. Today they are cultivated throughout the Tropics (FAOSTAT, 2005). The leaves of banana tree are large, flexible and waterproof. They are used in many ways, including as umbrella and to wrap food for cooking, carrying and packing cooked foods. In south India, foods are served only on banana leaves in households and hotels as well (Denham et al., 2003). Banana plant also has long been a source of fibre for high quality textile. Banana ash is known to be rich in potassium (Cordeiro et al., 2004). The potassium of banana leaf probably makes the milk alkaline and thereby inhibits degradation. Dutta and co-workers used banana rind, banana pseudostem and banana leaf as ash for removal of iron from groundwater (Dutta et al., 2007).

1.5 Problem statement

Several methods are available for color removal from wastewater such as aerobic and anaerobic degradation using various microorganisms, chemical oxidation, coagulation, flocculation, precipitation, filtration and reverse osmosis (Gulnaz et al., 2004; Sirianuntapiboon et al., 2006). However, these processes are costly and cannot effectively be used to treat wide range of such wastewater. All these methods have different color removal capabilities, capital costs and operating rates. On the other hand, adsorption (Nigam et al., 2002; Ozacar et al., 2005; Hameed et al., 2008) has been found to be a superior wastewater treatment compared to other techniques in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances (Robinson et al., 2002; Ardejani et al., 2007).

Currently, the most widely used and effective physical method in industry is activated carbon, although its running costs are expensive. This is mainly due to the chemicals required for regeneration after dye removal. Although activated carbon removes dyes from solution, they are then has to go through regeneration process which will increases the costs further. Therefore, the potential exists for the process of dye removal by adsorption to be more economically feasible by considering at the use of lower cost biosorbents (Robinson et al., 2001).

Several wastes and residues have been investigated for the adsorption of dyes with varying success. Therefore, new adsorbents which are economical, easily available and highly effective are still needed (Hamdaoui, 2006). The use of low-cost materials includes coirpith (Namasivayam and Kavitha, 2002), parthenium (Kardirvelu et al., 2003), coconut shell (Low and Lee, 1990), peanuthull (Periasamy and Namasivayam, 1996), rice husk (Nawar and Doma, 1989) and sugarcane baggase (Sugunadevi et al.,2002) have been considered as adsorbents for the removal of textile dyes. In this research new adsorbent is introduced as it is also considered locally available and minimize environmental problems associated with their built-up. Agricultural waste products are complex materials containing lignin and cellulose as its major constituents. Chemical adsorption can occur by the polar functional groups of lignin, which include alcohols, aldehydes, ketones, acid phenolic hydroxides and ethers which act as chemical bonding agents. Agro-based materials such as durian peel, pineapple stems, pineapple leaves, papaya stems, papaya leaves and banana leaves were selected as potential adsorbents for the investigation of adsorption of dye from synthetic wastewater.

1.6 Objectives of the research

This work was carried out to study the adsorption of methylene blue (MB) on agricultural solid wastes such as durian peel (DP), banana leaves (BL), pineapple stem (PPS), pineapple leaves (PPL), papaya stem (PYS) and papaya leaves (PYL) as alternative adsorbents in batch process. The objectives of the research are to:

1. Study the adsorption of methylene blue (MB) on agricultural solid waste (durian peel (DP), banana leaves (BL), pineapple stem (PPS), pineapple leaves (PPL),

papaya stem (PYS) and papaya leaves (PYL)) as alternative adsorbents in batch process. The effect of initial concentration, contact time solution pH and temperature on MB adsorption was investigated.

2. Study adsorption isotherm of MB on the different adsorbents.
3. Study the adsorption kinetic and thermodynamic of the adsorption process.

Chapter Two
Literature review

This chapter is organized into eleven sections which are dye structure, solution of dye, wastewater treatment, adsorption, factors effecting adsorption process, surface interaction, selectivity of adsorbent, adsorption isotherm, adsorption kinetics and thermodynamics.

2.1 Classifications of dyes

The classification by usage or application is the principal system. In many cases, a particular chemical class includes dyes of several application classes and particular application class may include dyes of varies chemical types (Robison et al. 2001)

- Reactive dyes
- Disperse dyes
- Direct dyes
- Vat dyes
- Cationic (basic) dyes
- Acid dyes
- Solvent dyes
- Sulfur dyes

Basic dyes are water-soluble and yield colored cations in solution. Water-soluble cationic dyes are applied to paper polyacrylonitrile, modified nylons and modified polyesters. Their original use was for silk, wool and tannin-mordanted cotton. The principal chemical classes are diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine and acridine (Hunger, 2003). Some basic dyes show biological activity and are used in medicine as antiseptics (Nunn, 1979).

2.2 Dye structure

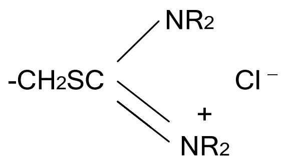
Dyes are chemicals which on binding with a material will give color to the material. Dyes are ionic and aromatic organic compounds with structures including arylrings which have delocalized electron systems. Basic dyes fall within the class of polymethines dyes (Allen, 2004). Dyes of different chemical structures are primarily based on substituted aromatic and heterocyclic groups such as aromatic amine (C_6H_5-NH_2) which is a suspected carcinogen, phenyl (C_6H-CH_2) and naphthyle (NO_2-OH). A large number of dyes are azo compounds (-N-N-) which are linked by an azo bridge (Raymond and Dunald, 1984). Dyes with simple structures and low molecular weights exhibit higher rates of color removal whereas color removal is more difficult with highly substituted high molecular weight dyes.

2.3 Solubility of dyes

2.3.1 Water-soluble dyes

Water solubility is expected to increase with increasing polarity and it follows that adsorption from aqueous solution generally decreases as polarity increases (Weber, 1985). A decrease in solubility acts to promote the attraction of the dyes to the adsorbent. Thus, nonpolar groups which have a low affinity for water usually increase the adsorption from aqueous solution (Derbyshire and Peters, 2009). Water solubility is conferred on many dyes by presence of at least one salt-forming group. The commonest of these is the intermediate compounds from which the dye is made but sometimes an insoluble dye is sulphonated. They are described as anionic dyes since it is the anion that is colored. The principle solubilizing groups used for commercial dyes are shown in Table.2.1.

Table 2.1: Solubilizing groups used with various classes of dyes (Parfitt and Rochester, 1983).

Permanent	
Inorganic Sulphonate $-SO_3^-\ Na^+$	Acid wool, direct cotton, chrome mordant 1:1 dye-metal complex wool dyes
Amino and quaternary ammonium $-NH_2HCl^-$, $-N^+R_3Cl$	Cationic dyes for cellulose, wool, silk and acrylic fibers
Polar Hydroxyl, amino, and sulphamide, $-OH$, $-NH_2$, $-SO_2NH_2$, etc.	Disperse dyes for synthetic polymer fibres and 2:1 dye-metal dyes for wool and nylon
Temporary	
Sodium phenolate, $-O^-Na^+$	Insoluble azo (azoic) dyes for cellulose (naphthlos coupled on the fibre with diazo compounds; vat dyes, later insolubilized by oxidation to quinine groups
isothiouronium 	Phthalocyanine dyes for cellulose

2.4 *Wastewater treatment*

In the textile industry, an area of major concern is the liquid waste stream from the dying process or from dye manufacturing processes. Such effluents contain leftover dyes and associated chemicals, which can create an economic loss and environmental concerns if the waste stream is not properly treated and the chemicals not recovered. Even in many cases where dyes are not toxic to the environment, they are unsightly when discharged to waterways. Treating dye bath effluent to remove color has proven difficult, because of the high temperature and harsh chemical environment of such waste streams.

Current processing schemes for dye-containing effluents include a variety of chemical treatments such as oxidation (Nansheng et al., 2007), neutralisation and destructive reduction. A variety of biological treatments (Annadurai et al., 2002), such as activated sludge, stabilization ponds, aerated lagoons, and trickling filters, and various physical treatments, such as carbon absorption, incineration, polymer flocculation, and sedimentation are also employed. In addition, reverse osmosis and ultra-filtration have also been used to treat dye waste streams, using of cellulose acetate, asymmetric polyamide or polyamide composites (John Wiley & Sons., 1993).

2.5 Methods of dyes removal

Methods of dye wastewater treatment have been reviewed by Banat et al. (1996), Slokar and Majcen Le Marachal (1998), Delée et al. (1998), Robinson et al. (2001) and Pokhrel and Viraraghavan (2004). Fungal and bacterial decolorization methods have been reviewed by Mcmullan et al. (2001), Fu and Viraraghavan (2001a), Stolz (2001), Wesenberg et al. (2003), Pearce at al. (2003) and Aksu (2005). The technologies can be divided into three categories: physical, chemical and biological (Robinson et al., 2001).

2.5.1 Physical methods

Different physical methods are also widely used, such as membrane-filtration processes (nanofiltration, reverse osmosis, electrodialysis, etc.) and adsorption techniques. In accordance with the very abundant literature data, liquid-phase adsorption is one of the most popular methods for the removal of pollutants form wastewater since proper design of the adsorption process will produce a high-quality treated effluent. This process provides attractive alternatives for the treatment of contaminated waters, especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application (Crini, 2006).

Adsorption is a well known equilibrium separation process and an effective method for water contamination applications (Dabrowksi, 2001). Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances (Crinci, 2006).

Decolourisation is a result of two mechanisms: adsorption and ion exchange (Slokar and Le Marechal, 1997), and is influenced by many physi-chemical factors, such as dye/sorbent interaction, sorbent surface area, particle size, temperature, pH solution and contact time (Kumar et al., 1998). The advantages and disadvantages of different methods used to remove dye from wastewater are summarized in Table 2.2.

Table 2.2: Advantages and disadvantages of the current methods of dye removal from industrial effluents (Robinson et al., 2001)

Physical/chemical methods	Advantages	Disadvantages
Fentons reagent	Effective decolourisation of both soluble and insoluble dyes	Sludge generation
Ozonation	Applied in gaseous state: no alternation of volume	Short half-life (20 min)
Photochemical	No sludge production	Formation of aromatic amines
NaOCl	Initiates and accelerates azo-bond cleavage	Release of aromatic amines
Cucurbituril	Good sorption capacity for various dyes	High cost
Electrochemical destruction	Breakdown compounds are non-hazardous	High cost of electricity
Adsorption by activated carbon	Good removal of wide variety of dyes	Very expensive
Adsorption by Peat	Good adsorbent due to cellular structure	Specific surface areas for adsorption are lower than activated carbon
Membrane filtration	Removes all type of dyes	Concentrated sludge production
Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Irradiation	Effective oxidation at lab scale	Requires a lot of dissolved O_2
Electrokinetic coagulation	Economically feasible	High sludge production

2.6 Adsorption

The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the *adsorbent*, and the material concentrated at the surface of the phase is the *adsorbate*. Adsorption is thus different from absorption, a process in which material transferred from one phase to another (e.g. liquid) interpenetrates the second phase to form a solution (Weber, 1972a).

In liquid phase adsorption process, molecules, ions or atoms in a liquid is diffused to the surface of a solid, where they bond with surface or are held there by weak intermolecular forces. The solid, which is insoluble in the liquid, is the adsorbent. The components being adsorbed are called solutes when in liquid and form the adsorbate upon adsorption on the solid. In general, the higher the concentration of the solute, the higher is the equilibrium adsorbate concentration on the adsorbent (Seader and Ernest, 1998). The maximum extent of adsorption occurs when equilibrium is reached.

Adsorption techniques have become favorable due to the efficiency in the removal of pollutions and stable conventional methods. Adsorption produces a high quality product, and is a process which is economically feasible (Choy et al., 1999). Adsorption has been used extensively in industrial process for many purposes of separation and purification.

The fundamental practical applications of adsorption are (Keller et al., 1987)

- Removal of colored and colorless organic pollutants from industrial wastewater
- Separation and purification of liquid and gas mixtures, bulk chemicals, isomers and air
- Drying gases and liquids before loading them into industrial systems

- Removal of impurities from liquid and gas media
- Recovery of chemicals from industrial and vent gases
- Water purification

The commercial adsorption processes for separating gas and liquid mixtures are accomplished due to selective adsorption of certain substances from their mixtures. The same idea is true for purification of gas and liquid mixtures and drying of some industrial gases. For those purposes the pore system of adsorbents used is sufficiently wide to enable fast diffusion, separation is caused mainly by selective adsorption that depends upon the Van der Waals forces between the adsorbents and the constituents of the gas or liquid mixtures. The above processes are major unit operations in the chemical and petrochemical industries (Dabrowski, 2001).

2.6.1 Types of adsorption

Adsorption may be classified into physical adsorption and chemical adsorption. They are differentiated by type of force between the fluid molecules and the molecules of solid. Here we will look at two types of adsorption which are physical and chemical adsorption.

(a) Physical adsorption

Physical adsorption or van der waals adsorption is caused mainly by van der waals forces and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent surface. Basically, it is a result of intermolecular forces of attraction between molecules of the solid and the substance adsorbed (Alley, 2007). It occurs when the intermolecular attractive forces between molecules of the solid and the liquid are greater than those between molecules of the liquid itself (Seader and Ernest, 1998).

Physical adsorption is usually predominant at low temperature and characterized by a relatively low energy of adsorption that is adsorbate is not held as strongly to the adsorbent as for chemical adsorption. The reversibility of physisorption is dependent on the strength of attractive forces between adsorbate and adsorbent.

(b) Chemical adsorption

Chemical adsorption also known as chemisorption or activated adsorption is the result of chemical interaction between the solid and the adsorbed substance. The strength or the chemical bond may vary considerably, and identifiable chemical compounds in usual sense may not actually form. But the adhesive force is generally much greater than that found in physical adsorption. The process is generally much irreversible and the heat liberated during chemisorption is usually large (Kenneth et al., 1991).

A major application of the adsorption process is for discoloration of sugar solutions and other foods by bone char then proceed to the later implementation of activated carbon for removing undesirable gases from the battlefield (Slejko, 1985). Nowadays, the adsorption phenomena have become constructive method for decontamination, purification and separation processes. Adsorption phenomena are operative in most natural physical, biological, chemical systems (Furuya et al., 1997). The differences between physical and chemical adsorption are best illustrated in Table 2.3.

Table 2.3 Comparison of physical and chemical adsorption (Ruthen,1984; John and Joaquim, 1993).

Parameter	Physical adsorption	Chemical adsorption
Adsorption enthalpy (kcal/mol)	<10	>20
Adsorption rate	Diffusion controlled	Controlled by the surface chemical reaction
Specificity	Low	High
Interaction	Reversible	Irreversible
Surface covered	Complete	Incomplete
Activated energy	Small	Large
Adsorption/ energy of adsorbent	Large	Small
Adsorption site	Monolayer or multilayer	Monolayer only
Nature of adsorption	No dissociation of adsorbed species	May involve dissociation
Temperature	Only significant at relatively low temperature	Possible over a wide range of temperature
Electron transfer	No electron transfer although polarization of sorbate may occur	Electron transfer leading to bond formation between sorbate and solid surface

2.7 Factors affecting adsorption process

2.7.1 Adsorbate

The chemical character of the adsorbate is important for a number of reasons. It is this character which determines the size as well as the configuration of the particular molecule to be adsorbed. Molecular size is important for two reasons. First, for any homologous series of organic molecules, as size increases solubility generally decreases. A material which has low solubility in water will have a higher affinity for solid surfaces than for the water and will have a tendency to concentrate on those surfaces to adsorb. Molecular size is also important for the perspective that all adsorbents depend upon internal surface area for the full use of their adsorption capabilities (Abdullah et al., 2005). If the molecular size is too large, adsorption will be hindered and adsorption capacity will decrease. A very large molecules will block or cannot penetrate pores or pathways within the adsorbent. One further aspect of molecular size is that larger molecules will tend to diffuse more slowly from solution and therefore will require longer times for full equilibrium adsorption capacity to be realized (Alley, 2007).

The molecular form of the particular adsorbate is also of significance. Whether the molecule is in an ionic or neutral state, whether it is a branched isomer or straight chain, it can have significant effect on the removal of this material from solution by adsorption. The molecule form can have consequences affecting the solubility of the adsorbate and it can also determine the energy of adsorption, the force with which the particular molecule is held on the adsorbent. Furthermore, these characteristics can affect the rate of diffusion of the molecule through the liquid. The rate of diffusion is usually a function of both molecular size and form for a given solvent (Faust and Aly, 1998).

2.7.2 Solution

The three major solution characteristics which have particular impact on adsorption are: the solution pH, its temperature and the presence of other competing adsorbate compounds.

(a) Solution pH

Solution pH has a significant effect on the adsorbent as well as on the adsorbate. Both adsorbent and adsorbate may have chemical characteristics which are affected by the concentration of hydrogen (H^+) in the solution. Some adsorbent have affinity for H^+ or OH^- and can directly affect the solution pH and therefore solubility and adsorption capacity (Faust and Aly, 1998). In addition, other ions in the system may thus be influenced by solution pH. A change in ionization can drastically affect the overall adsorption process. pH of solution primarily affects the degree of the phenolic sorbate in adsorption process (Aksu and Yener, 2001). Ionization is normally unfavorable to adsorption by carbon or any means of adsorbent. However, this excluded the case for hydrogen ion, which significantly adsorbed under certain condition. There are some negative ions, which are more sorbable when associated with H^+. A low pH promotes the adsorption of organic acids whereas a high pH would favor the adsorption of organic bases (Faust and Aly, 1998).

Adsorption from solution can be highly pH sensitive in aqueous system where an adsorbate exhibits an isoelectric point or neutral point on the pH scale. It is at this point where maximum adsorption can be achieved since solubility is minimized and non polar adsorbent has greatest affinity for non-ionic materials. Ho and Ofomaja, (2006) reported that the biosorption process capacity of copra meal was low at the initial pH 3 but increased and remained almost constant over the pH ranges of 5-7. Hameed (2009) reported the sorption of MB was minimum at the initial pH 3 and increased with pH up to 5 and then remained constant over the initial pH ranges of 5-10. Several studies on pH effect on the adsorption process are summarized in Table 2.4.

Table 2.4 Studies on effect of pH on adsorption process.

Adsorbent	Adsorbates	Dyes removal	References
Activated sludge	Basic blue 9 Basic red 18	Increases	Gulnaz et al., (2004)
Sludge ash	Methylene blue	Decreases	Weng and Pan, (2006)
Rice straw-derived char	Malachite green	Increases	Hameed and El-Khaiary, (2007)
Hazelnut shells	Methylene blue	Increases	Ferrero, (2007)
Papaya seeds	Methylene blue	Increases	Hameed, (2008)
Grass waste	Methylene blue	Increases	Hameed, (2009)
Pine-fruit shell	Methylene blue	increases	Royer et al., (2009)
Moroccan clay	Basic red 46	Increases	Karim et al., (2009)

(b) Temperature of solution

The temperature of a solution has two major effects on adsorption. First, the rate of adsorption is usually increased at higher temperature. This is due primarily to the increased rate of diffusion of adsorbate molecules through the solution to the adsorbent. Further, since solubility and adsorption are inversely related, as temperature affects solubility it will therefore affect the extent of adsorption or capacity of the adsorbent for the particular adsorbate. The adsorption process at any particular concentration decreases with increasing of temperature which is normally an exothermic process (Crini and Badot, 2008).

Ozcan and Ozcen reported that the amount of acid red 57 dye adsorbed on sepiolite decreases with the increasing of temperature from 20 ^{o}C to 50 ^{o}C. Gulnaz et al., (2004) reported that the adsorption capacities of dried activated sludge increased with decreasing temperatures from 50 ^{o}C to 20 ^{o}C which indicated that the adsorption process was exothermic. The sorption capacity of dried activated slugde were determined as 73.2, 60.1 and 43.6 mg/g for basic red 18 dye and 61.2 and 33.6 mg/g for basic blue 9 dye at 20, 35 and 50 ^{o}C, respectively.

Wu et al., (2001) studied the adsorption of one basic blue 69 (BB69) onto activated clay in the temperature range 15-75 ^{o}C. They reported that adsorption capacity of BB69 dye on activated clay increased with increasing temperature, the adsorption of BB69 was extremely favorable. Several studies of endothermic and exothermic nature of adsorption process are summarized in Table 2.5.

Table 2.5 Studies reported by researchers on temperature effects on adsorption process.

Adsorbents	Adsorbates dyes	Temperature (^{o}C)	Endo-thermic	Exo-thermic	References
Sahara desert sand	Methylene blue	30-60		√	Varlikli et al., (2009)
Pineapple leaf powder	Methylene blue	4-54		√	Weng et al., (2009)
Activated carbon – coconut husk	Methylene blue	30-50		√	Hameed et al., (2007)
Calcium alginate beads	Basic black	30-70	√		Rao et al., (2007)
Wheat shells	Methylene blue	30-50	√		Bulut and Aydin, (2006)
Australian natural zeolite	Methylene blue	30 and 50	√		Wang and Zhu, 2006
Sewage sludge and discarded tyres	Methylene blue	15-50	√		Rozadaa et al., 2005

(c) Presence of other competing adsorbate compounds

A major influence of the solution character on adsorption is the presence of competing adsorbate compounds. Few adsorbents demonstrate controllable selectivity for specific compounds and therefore all absorbable compounds present will compete for adsorption sites. Further, since physical adsorption is a reversible phenomenon, the presence of materials with of lesser affinity will effect adsorption process. This effect can result in what is known as a chromatographic effect can have particularly dramatic consequences for the quality of an effluent (Slejko, 1985).

Chiou and Chuang (2006) reported that the presence of other molecules might affect the adsorption of a particular molecule. They concluded that several dyes in a solution would compete against each other for available sites. Those having the greatest ionic potential would be removed first, and if the sites were still unsaturated, then those having lower ionic potential would be removed in sequences. The more electronegative molecules are attracted to the surface more strongly. Although the presence of more than one dye in a solution creates competition for adsorption sites, the total adsorption capacity has been found to increase.

2.8 Adsorbent

The chemical and physical properties of the adsorbent used to remove a material from solution are quite important.

(a) Physical properties

The physical properties of the adsorbent are like-wise important. The adsorbent can be in the form of granules or particles which may have a density near or very different from the solution to be treated; or the adsorbent may be in very fine powdered form which may be easily suspended in the solution to be treated. These