PRODUCTION AND CHARACTERIZATION OF SILICA GEL FOR TEXTILE WASTEWATER TREATMENT (METHYLENE BLUE DYE)

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Symbol	Abbreviations
A	The Temkin isotherm constat (L/g)
A^O	Angstrom = 1.0 x 10^{-10} metrs
A_O	Absorbance of methylene blue in the sample solution before treatment
Abs.	Absorbance
A_e	Absorbance of methylene blue in the sample solution after treatment
B	Dimensionless Temkin constant
b	Temkin constant related to heat of sorption (j/mol)
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
C_o	Concentration of methylene blue in the sample solution before treatment
C_e	Concentration of methylene blue in the sample solution after treatment
C_i	Intial concentration of methylene blue in the sample solution (mg/L)
ε	Absorptivity (extinction coefficient)
FT-IR	Fourier Transform Infrared
XRD	Lagergren's first order constant
K_1	X-ray diffraction
K_2	The pseudo second order constant
K_d	The distribution constant
K_F	Freundlich constant which is an approximate indicator of adsorption capacity of the sorbent (mg/g $(L/mg)^{1/n}$
K_L	Langmuir isotherm constant (L/mg)
m_{ads}	Mass of adsorbent dose
n	Dimenshionless Freundlich constant giving an indication how favourable the adsorption process
Q_e	The amount of Methylene blue dye adsorbed per gram of adsorbent
Q_m	Maximum monolayer coverage capacity (mg/g)
Q_t	The amount of Methylene blue dye adsorbed per gram of adsorbent at a time t

R^2	Correlation coefficient
R	The gas constant
R_L	Correlation coefficient
T	Time
T	The absolute temperature ^{O}K
V	Volume of solution
ΔG^O	Standard free Gibbs energy
ΔH^O	Standard enthalpy
ΔS^O	Standard entropy
K_{id}	The intra-particle diffusion coefficient
WHO	World Health Organization

Abstract

In the world, different pollutants from industries released every day to the soil and ground water without treatment. This will lead to different health problems to both human beings and animals. According to pure earth non-profit environmental organization, because of pollution more than 200 million peoples was affected. In some of the world's most polluted places babies are born with birth defects, children have lost 30 to 40 IQ points, and life expectance may be as low as 45 because of cancer and other diseases. In Ethiopia most textile factories are located nearby water bodies and they discharge their colour effluent to canals, rivers, lakes and streams without treatment. Those effluents have the capacity to cause an adverse effect on all forms of livings. Among those dyes discharging MB dye without treatment can affect human life and aquatic life. To protect human life as well as aquatic life the product silica gel (SiO_2) was successfully prepared from sodium silicate solution and sulphuric acid by sol-gel process to treat dye house waste. The obtained dry silica gel is characterized by using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The variables pH of silicic acid sol and pH of quenching water was studied by using design expert 7.0.0 software. A 2 Factorial model was adopted in order to represent the results in the form of three-dimensional surfaces. The results showed that the pH of silicic acid sol effect is more significant than pH of quenching water. We obtained gels with a good adsorption capacity of MB dye 48.84 mg/g at pH of silicic acid sol 3 and pH of quenching water is acidic (4). The adsorption experiments were conducted at different particle size, wide range of pH, adsorbent dosage, temperature, initial concentration, and contact time to adsorb MB dye efficiently. It was observed that around 78.8 % removal efficiency of MB day was achieved after 15 min, at solution pH around 10.06 and 25 ^{O}C temperature using 0.02 g weight of dose of silica gel with particle size $\leq$ 100 μm and intial concentration of 20 mg/L of 50 ml dye solution. Different adsorption isotherm models, adsorption kinetics and adsorption thermodynamics are carried out to determine the maximum adsorption capacity, to identify feasibility and favourability of using silica gel for adsorption of MB dye. Langmuir maximum adsorption capacity Q_m is 58.45 mg/g, at 25 ^{O}C and pH 10.06 and 0.02 weight of adsorbent dose. The R_L value (0.185 at 25 ^{O}C) indicates that the adsorption of MB dye on silica gel is favourable. From Freundlich isotherm model parameters, value of 1/n = 0.6452 while 1/n = 1.55 indicating that the sorption of MB dye on silica gel is favourable. The negative ΔG^{O} values (-1067.82 to -1959.0 J/mol) indicates that the adsorption is favourable and spontaneous at these temperatures. The positive value of ΔS^{O} (39.45 J/mol.K)

suggests that some structural changes occur on the adsorbent and the randomness at the solid/liquid interface in the adsorption system increase during the adsorption process. So the above methods give us silica gel is an effective adsorbent for treating industrial wastewater polluted with methylene blue under alkaline, low concentration of MB dye at temperature around 25^{O}C for removal over 85 %.

1. INTRODUCTION

1.1 Background

The process of making land, water, air or other parts of the environment dirty and unsuitable to use as a result of the introduction of pollutants in to the natural environment is called pollution.

Human are dependent upon ecosystem services such as air, water and food for survival. Statistical figures reveal that more than 70 percent of the surface of the Earth is covered with water. However, a large proportion of this water is not suitable for human consumption due to water pollution. This is due to the increase in population, growth of industries, urbanization, lack of environmental awareness, use of chemical fertilizers instead of organic manures, untreated effluent discharge from industries and municipalities, introduction of chemicals and dangerous foreign material including chemicals, swages, pesticides and fertilizers from agricultural runoff, or metals like lead and mercury entered to the receiving water.

According to pure earth non-profit environmental organization because of pollution more than 200 million people was affected. In some of the world's most polluted places babies are born with birth defects, children have lost 30 to 40 IQ points, and life expectance may be as low as 45 because of cancer and other diseases. Developing nations are likely to be affected more severely by the shortage of water as well as water pollution, where already almost 80 percent of health illness is directly or indirectly related with water quality.

Many industries are providing employment, increasing local income and earning foreign exchange for the development of country. However, these industries discharge their waste into the ecosystems without treatment which adversely affecting livelihood and day to day life. The industrial wastewater may have undesirable color, odour, taste, organic matter, harmful chemicals, toxic metals, total dissolved solids, acids, alkalis, virus, bacteria, worms and industrial waste products. Pollution caused by agents such as heavy metals and dyes are amongst the list which rendered the environment unwholesome and posed serious health concern to the populace.

The treatment of industrial wastewater has become more important in recent years as industrial effluents contain many toxic pollutants, such as dyes, which can severely damage the environment (Ho et al. 2000; Huang et al. 2011b). There are over 100,000 commercially available dyes with over 7×10^5 tonnes of dyestuff are produced annually. Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries. The total worldwide consumption of dyes by the textile industries is in excess of 10^7 kg per year, and approximately one million kilograms of dye are discharged into rivers and streams by textile industries each year (Órfão et al. 2006; Demirbas 2009; Huang et al. 2011b). The major problem associated with the discharge of large quantities of these organic compounds in wastewater is their chemical stability and low biodegradability in water due to their complex aromatic structure and synthetic origin, which is potentially harmful to the environment. Also many of them are known to be toxic or carcinogenic (Crini and Badot 2008; Fatimah et al. 2011).

Color stuff discharged from industries poses certain hazards and environmental problems. These coloured compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and affecting aquatic ecosystem. Furthermore, many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities. The discharge of industrial wastewater cause serious environmental problems due to their chemical structure gives them a persistent and recalcitrant nature.

In Ethiopia, the textile industries have great economic significance by virtue of its contribution to overall industrial output and employment generation when compared to other industries such as leather, paper, pulp and food industries.

Textile wastewater contains non-biodegradable organic and inorganic materials such as dyes, metals, phosphates, aerosols, high COD and BOD concentration, surfactants and phenols. Due to usage of dyes and chemicals, effluents are dark in color, which increase the turbidity of the water body. This affects the photosynthesis process and affects the habitat (Joseph Egli 2007). Nowadays, dyes mainly consists aromatic and heterocyclic compounds, with color imparting group and polar groups. The structure is more complicated and stable, resulting in greater difficulty to degrade the printing and dyeing wastewater (Ding etal 2010).

Many types of dye such as direct, reactive, acid and basic dyes are used in textile industries. Most of these dyes represent acute problems to the ecological system as they considered toxic and have carcinogenic properties, which make the water inhibitory to aquatic life. Due to their chemical structure, dyes possess a high potential to resist fading on exposure to light and water. The main sources of wastewater generated by the textile industry originate from the washing and bleaching of natural fibres and from the dyeing and finishing steps. But most of them lack effluent treatment plants. Instead, they directly discharge untreated colored dyes and toxic effluent into the nearby canals, rivers, lakes, and streams.

Methylene blue (MB) is one of the most commonly used substances for dyeing cotton, wood and silk. Though MB is not strongly hazardous, it can cause some harmful effects where acute exposure to MB will cause eye burns, increased heart rate, vomiting, shock, cyanosis, jaundice, and quadriplegia and tissue necrosis in humans, tachycardia, if inhaled. It also causes irritation to the skin. Hence it is necessary to remove MB from wastewater (K.V. Kumar, A . Kumaran, J. Biochem. Eng.2005). Various physical, chemical and biological techniques, such as ultrafiltration, reverse osmosis, ion exchange and adsorption on various adsorbents have been developed for removing dye from aqueous solutions (Huang et al. 2011). Chemical techniques are often expensive and the accumulation of concentrated sludge from which dye has been removed presents a disposal problem. In addition, a secondary pollution problem may arise due to the excessive use of chemicals (Karim et al. 2012). Adsorption is one of the most attractive technologies because it is highly efficient, cheap and easy to use (Debnath et al. 2013). The key aspect of adsorption technology is an excellent adsorbent with high adsorption capacity, rapid adsorption kinetics as well as high selectivity for adsorbates during the adsorption process. Various traditional adsorbents, such as zeolite, clay, activated carbon, fly ash, peat, microbial biomass and agricultural residues have been used for removing dye from wastewater. Inherent disadvantages of these materials are their low loading capacities, relatively small dye binding constants and poor selectivity (Zhuang et al. 2009; Huang et al. 2011a; Debnath et al. 2013).

Over the past two decades, silica gel have received extensive attention as promising adsorbents with a wide field of applications due to their high surface area, tunable and uniform pore structure, high pore volume, ordered pore structure, thermal and mechanical stability and extraordinarily wide possibilities for functionalization . In recent years, silica gels have been used to adsorb heavy metal ions ions (Agua-do et al. 2009; Li et al. 2011; Addy et al. 2012; Shahbazi et al. 2013; Shahbazi et al. 2014) , organic dyes (Pugazhenthi 2009; Qin et al. 2009; Huang et al. 2011a; Huang et al. 2011b; Boukoussa et al. 2013; Badiei et al. 2014), polycyclic aromatic hydrocarbons (Choudhary and Mantri 2000; Dou et al. 2011; Vidal et al. 2011; Balati et al. 2014), and other organic pollutants and the results indicate that silica gel have excellent adsorption ability (Kim et al. 2011; Najafi et al. 2012). There are a few studies on the use of silica gel for adsorbing dyes, mainly because silica gel were first synthesized in the early 1990s. In addition, these materials have rarely been used for treating wastewater.

The aim of this paper is production of an adsorbent called silica gel from sodium silicate and sulphuric acid those are produced in our country (Ethiopia) by using sol-gel method for effective adsorption of methylene blue dye and also study economic feasibility and favourability of using silica gel as an adsorbent to adsorb MB dye specifically.

The data on the use of characterized silica gel for adsorbing MB dyes is reviewed. The effects of various parameters, such as the process variables and experimental conditions are presented and discussed. The equilibrium and kinetic models which are used to characterize the adsorption processes are also reviewed.

1.2 problem Statement

In Ethiopia there are 109 firms engaged in manufacturing textile and apparel. Among this industries 104 of them are owned by the privet sector and the rest are under state ownership. And almost all are located very near to fresh water bodies. In textile processing about 16% water consumption is in the dye-house processing. From the total waste water effluents discharged from these textile industries this processes covers 15% - 20%. Since most of them use synthetic dyes rather than natural dyes effluents constitute large quantities of synthetic dyes. Due to the complexity of these synthetic dyes discharging them without treatment have the capacity to produce an adverse effects on all forms of livings like soil, water, flora, fauna, livestock and human population. Among those dyes Methylene blue (MB) is one of the most commonly used substances for dyeing cotton, wood and silk. Discharging MB day without treatment will cause eye burns, increased heart rate, vomiting, shock, cyanosis, jaundice, and quadriplegia and tissue necrosis in humans. But most of textile industries lack effluent treatment plants. Instead, they directly discharge untreated colored and toxic effluent into the nearby canals, rivers, lakes, and streams.

1.3 Objectives

1.3.1 General objective

The general objective of the study was production and characterization of silica gel for removal from textile dye-house wastewater by adsorption process.

1.3.2 Specific objectives

The specific objectives were to:

- ✓ Synthesis of silica gel from Ethiopian sand
- ✓ Study the effect of pH of silicic acid sol and pH of quenching water on Methylene Blue dye adsorption capacity of silica gel.
- ✓ Characterize silica gel using XRD and FTIR test.
- ✓ Observe the effect of adsorbent dose, solution pH, adsorption temperature, solute concentration, particle size and contact time on methylene blue removal capacity of silica gel.
- ✓ The feasibility of using silica gel for adsorption of a methylene blue.

1.3 Significance of the study

The acute exposure to methylene blue has been found to cause increased heart rate, cyanosis, vomiting, shock, heinz body formation, jaundice, quadriplegia and tissue necrosis in humans and also discharging MB from textile industries in the ecosystem is a dramatic source of non-aesthetic pollution, eutrophication and perturbation in the aquatic life. The goal of this project work is synthesis of an adsorbent called silica gel from Ethiopian sand due to its high adsorption capacity, high surface area, microporous structure, and technically easier sorption of methylene blue from textile wastewater effectively to protect human, animals and aquatic life's from acute exposure to methylene blue.

2. LITERATURE REVIEW

2.1 Methylene blue dye

2.1.1 Structure and property

Methylene blue is a heterocyclic aromatic compound with molecular formula $C_{16}H_{18}ClN_3S$ as shown in Figure 2.1, with IUPAC name ***3,7-bis(Dimithylamin)-phenothiazin-5-ium chloride.*** Methylene blue (MB) is a cationic thiaizine dye that is deep blue in the oxidized state while it is colorless in its reduced form leucomethylene blue (Miclescu A. and Wiklund L. 2010) Chemical and physical properties of Methylene blue is summarized in Table 2.1 (Tani A., Thomson A. and Butt J., 2001).

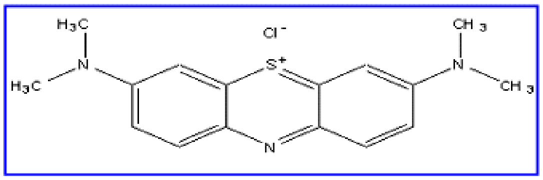


Figure 2. 1: Intra-particle Diffusion

Table 2. 1Chemical and physical properties of MB dye

Chemical and physical properties	Values
Melting Temperature	180^{o}C
Boiling Temprature	No data
Solublity in water	35.5 g/L
PH value	3(10 g/L H_2O)
Molocular weight	319.09 g/mol
Color	Dark blue-green in oxidized form,colorless in reduced form (leucomethylene blue)
Chemical formula	$C_{16}H_{18}ClN_3S$

2.1.2 Industrial and medicinal uses of Methylene Blue

MB dye is used in dye, paint production and wool dying. Many dyes are widely used in different industries, such as textile, paper, rubber, plastic, leather, food and pharmaceutical. Medicinal use of MB include therapeutically in the treatment of methemoglobinemia and cyanide poisoning. Other medicinal uses of methylene blue include the management of chronic urolithiasis and treatment of cutaneous viral infections as well as the treatment of manic-depressive psychosis.

2.1.3 Toxicological effects of Methylene Blue dye on human and animals:

2.1.3.1 Toxicological effects on human:

Acute exposure to methylene blue has been found to cause increased heart rate, cyanosis, vomiting, shock, Heinz body formation, jaundice, quadriplegia and tissue necrosis in humans. In addition, corneal and conjunctival injury has been reported following acute exposure to this compound. Intravenous administration of methylene blue has been found to cause bluish discoloration of the urine and stool. Numerous case reports were found in the literature describing the effects of methylene blue on the newborn, following the injection of this compound into the amniotic fluid before delivery. At birth, many of the infants reportedly had deep blue stained skin and voided blue urine. Other symptoms including respiratory distress, hyperbilirubinemia, methemoglobinemia, Heinz body formation and increased heart rate occurred after birth. No data were found on the prechronic effects of methylene blue in humans. Chronic application of methylene blue-containing eye drops has been found to result in staining of the bulbar and palpebral conjunctiva, the lid margins and slight staining of the corneal epithilium. No other data were found on the chronic/carcinogenic effects of methylene blue in humans. Methylene blue has been found to cause an elevation in follicle stimulating hormone and estradiol in fallopian tube secretions, and uterine and peritoneal fluids in vitro. In addition, methylene blue was found to significantly inhibit sperm motility in vitro in samples prepared from human semen. No other studies were found on the reproductive effects of methylene blue in humans. (Arthur D. Little 1990).

2.1.3.2 Toxicological effects on animal:

Numerous reports were found in the literature describing the association between methylene blue and the formation of Heinz bodies in animals. Intraperitoneal administration of methylene blue has been found to induce Heinz body formation in cats, dogs, mice and rabbits. In cats, methylene blue was observed to cause bluish stained skin, anemia, discolored urine, dyspnea, depression, respiratory stimulation and increased blood pressure. In addition, methylene blue has been found to cause corneal and conjunctival injury in rabbits. No data were available on the prechronic, effects of methylene blue in animals. Administration of this compound at a concentration of 4% in the diet for 2 years was not found to induce tumor formation. Methylene blue has been found to inhibit the ability of mouse embryos to grow and cleave in vitro. This compound also caused an increase in implantations and resorptions in litters born to rats fed diet containing methylene blue. MB toxicity has occurred at a wide range of doses. Dose-related toxicity of MB is summarized in Table 2.2 (Miclescu A. 2009)

Table 2. 2 Dose related toxicity of MB dye

Animal studies	**Toxic doses (mg/Kg)**	**Manifestation**
Rat	5-50	Neuronal apoptosis, reduced MAC isoflurane
Dog	10-20	Hypotension, decreased SVR,renal blood flow, pulmonary hypertension
Human studies	**Toxic doses (mg/Kg)**	**Toxic Manifestation**
	2-4	Hemolytic anemia, skin desquamation in infants
	7	Nausea, vomiting, abdominal pain, chest pain, fever, hemolysis
	7.5	Hyperpyrexia, confusion
	20	Hypotension
	80	Bluish discoloration of skin (similar to cyanosis)

2.2 Textile dyeing effluent

Textile and garment has been an important sub sector as it serves basic human needs by providing cloth and other basic textile needs. It offers employment for masses of the world's peoples, which is estimated to be at least 40 million (Mamo, 2004). Especially, the clothing industry is labour intensive and it offers entry-level jobs of unskilled labour in developed and developing countries. Moreover, it is a sector where relatively modern technology can be adopted even in poor countries at relatively low investment costs. These technological features of the industry have made it suitable as the first rung on the industrialization ladder in poor countries, some of which in particular in Asia, have experienced a very high output growth rate in the sector (Nordas, 2004).

The history of modern textile industry in Ethiopia goes back to the late 1930's with the establishment of the first textile factory, Dire Dawa Textile. Join venture investments with Italian, Japanese, Indian and British companies were instrumental in the early development of the textile industry (Mulat, et.al., 2004:40). Ethiopian textile and garment sub-sector is the third largest manufacturing industry, only later than the food processing and beverage and leather industry. Currently, Ethiopian textiles and apparel industry encompasses spinning, weaving, finishing of textiles, manufacture of cordage, rope, twine, netting, knitting mills, and manufacturing of wearing apparel. The firms in the industry produce products such as cotton and woolen fabrics, nylon fabrics, acrylic and cotton yarn, blanket, bed sheet, shirts, carpets, gunny bags, wearing apparels, and sewing thread. Ethiopia has slightly over a hundred textile and apparel units of medium and large size scale; within which there are sixteen textile processing units (the majority of which are integrated down or up the value chain) that can process natural and synthetic textile materials of different forms using machineries ranging from state of the art technology to semi-automated ones. According to CSA survey of the Ethiopian manufacturing sector in 2012/13, there were 109 firms engaged in manufacturing of textile and apparel, most of them are owned by private, which is 104 and the rest five firms are under state ownership

The cynical effect of textile industry is, consuming dyes particularly harmful synthetic dye such as azo dyes for dyeing and coloring process. Ancient time's natural dyes are typically applied for dyeing process though these processes provided a limited range of colors on fabrics and it appears dull shade so these dyes are not much attractive by the people. The negative aspect of using natural dyes on fabric is easily faded when exposed to sunlight and washing as a result the synthetic dyes are successfully entered into the industrial market particularly textile industry. Synthetic dyes are complex substances most of them have produce an adverse effects on all forms of livings like soil, water, flora, fauna, livestock and human population.

Approximately calculating that 80,000 tons of dyes used in various industries such as food processing industries, cosmetics, paper mills etc but the textile division alone consumes about 60% of total dye production for coloring a variety of fabrics and about 10–15% of unspent dyes are let out into the clean water bodies which makes the water highly coloured and polluted, typically with a concentration range 10–200 ppm.

Large quantities of water are needed for textile processing, dyeing and printing. Among these various processes, dyeing process includes fixing dyes on fabrics, washing etc requires more water and it consumes 16% of total water usage depending on the type of dyes used and this dyeing sector contributes to 15% - 20% of the total waste water flow. According to WHO nearly 80% of water is polluted in developing country due to the dumping of domestic waste into aquatic bodies. Particularly in India almost 70% of the water has become polluted due to the discharge of domestic sewage and industrial effluents into natural water source, such as rivers, streams as well as lakes. The colour, concentration of trace metals, nature of dyes, and characteristics of effluent vary from industry to industry based on the water utilization and every day manufacturing goods. Major pollutants released from the textile industries are from the several of their wet- processing operations like scouring, bleaching, mercerizing and dyeing. The release of those colored waste waters in the ecosystem is a dramatic source of non-aesthetic pollution, eutrophication and perturbation in the aquatic life.

2.3 Methods of treatment for removing dyes

The textile industry is one of the greatest generators of liquid effluent pollutants, due to the high quantities of water used in dyeing processes. Several methods are used for removing dye from wastewater. Technologies can be divided into three categories: biological, chemical and physical. Biological treatment is often the most economical alternative to physical and chemical processes. However, application of biological treatment is often restricted because of technical constraints. Biological treatment requires a large land area and is constrained by diurnal variation and toxicity of some chemicals and the inflexibility of the design and operation.

The most important disadvantage of chemical methods is the production of sludge resulting from the use of chemicals and in addition, the disposal of the sludge is expensive. There is also the possibility that a secondary pollution problem will arise because of the excessive use of chemicals. Adsorption is globally recognized as the most promising method of wastewater treatment because of its versatility, wide applicability and low cost. Most adsorbents are easily available and inexpensive. However, their practical application has been limited by problems associated with their regeneration, disposal, poor mechanical stability, high sludge production and low removal effectiveness of a wide range of dyes. To overcome these disadvantages, which are a major challenge for dye removal, various nano-adsorbents have been developed. After 1995, some attempts were made to prepare and use these nano-sized materials to simply remove dyes from aqueous systems.

An early attempt was that of Wu and co-workers, who adsorbed several anionic dyes on nano-sized alumina modified silica particles of different compositions. Among nano-adsorbents, nano structure materials such as MPSs have been found to be suitable adsorbents for the removal of dyes from wastewater. MPSs offer significant improvements over conventional adsorbents with their extremely high specific surface area, short intraparticle diffusion distance, tunable pore size, changeable surface chemistry and high adsorption capacity. (Shahbazi A. and Salahshoor Z.)

2.4 Adsorption

There are several examples, which reveal that the surface of a solid has the tendency to attract and retain the molecules of the phase with which it comes into contact. These molecules remain only at the surface and do not go deeper into the bulk. The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption. The molecular species or substance, which concentrates or accumulates at the surface is termed adsorbate and the material on the surface of which the adsorption takes place is called adsorbent. Adsorption is essentially a surface phenomenon. Solids, particularly in finely divided state, have large surface area and therefore, charcoal, silica gel, alumina gel, clay, colloids, metals in finely divided state, etc. act as good adsorbents.

2.4.1 Distinction between adsorption and absorption

In ***adsorption***, the substance is concentrated only at the surface and does not penetrate through the surface to the bulk of the adsorbent, while in absorption; the substance is uniformly distributed throughout the bulk of the solid. For example, when a chalk stick is dipped in ink, the surface retains the colour of the ink due to adsorption of coloured molecules while the solvent of the ink goes deeper into the stick due to absorption. On breaking the chalk stick, it is found to be white from inside. A distinction can be made between absorption and adsorption by taking an example of water vapour. Water vapours are absorbed by anhydrous calcium chloride but adsorbed by silica gel. In other words, in adsorption the concentration of the adsorbate increases only at the surface of the adsorbent, while in absorption the concentration is uniform throughout the bulk of the solid.

Both adsorption and absorption can take place simultaneously also. The term sorption is used to describe both the processes.

2.4.2 Mechanism of adsorption

Adsorption arises due to the fact that the surface particles of the adsorbent are not in the same environment as the particles inside the bulk. Inside the adsorbent all the forces acting between the particles are mutually balanced but on the surface the particles are not surrounded by atoms or molecules of their kind on all sides, and hence they possess unbalanced or residual attractive forces. These forces of the adsorbent are responsible for attracting the adsorbate particles on its surface. The extent of adsorption increases with the increase of surface area per unit mass of the adsorbent at a given temperature and pressure.

Another important factor featuring adsorption is the heat of adsorption. During adsorption, there is always a decrease in residual forces of the surface, i.e., there is decrease in surface energy which appears as heat. Adsorption, therefore, is invariably an exothermic process. In other words, ΔH of adsorption is always negative. When a gas is adsorbed, the freedom of movement of its molecules becomes restricted. This amount to decrease in the entropy of the gas after adsorption, i.e., ΔS is negative. Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system. For a process to be spontaneous, the thermodynamic requirement is that, at constant temperature and pressure, ΔG must be negative, i.e., there is a decrease in Gibbs energy. On the basis of equation, $\Delta G = \Delta H - T\Delta S$, ΔG can be negative if ΔH has sufficiently high negative value as – TΔS is positive. Thus, in an adsorption process, which is spontaneous, a combination of these two factors makes ΔG negative. As the adsorption proceeds, ΔH becomes less and less negative ultimately ΔH becomes equal to TΔS and ΔG becomes zero. At this state equilibrium is attained.

2.4.3 Types of adsorption

The process of adsorption is divided into Physiorption and Chemisorption depending on type of forces involved between adsorbent & adsorbate

A) *Physiorption:* It involved intermolecular force of attraction. It is based on the fact that there is a concentration gradient of adsorbate in solution & adsorbent so that adsorbate migrates from solution into the pores of adsorbent to reach the point of maximum force of attraction & thus get adsorbed.

B) *Chemisorption:* It involves chemical bonding between the adsorbent & adsorbate molecule. The chemical bonds may be covalent or ionic in nature. In general most of the solids have a property to adsorb the solute from solution but few of them are actually used commercially. Among this activated carbon, Silica gel and activated alumina are used extensively.

2.4.4 Adsorption isotherms models

The modelled adsorption isotherm is an invaluable non-linear curve describing the adsorption phenomenon at a constant temperature and pH; and the mathematical correlation which is depicted by the modelling analysis is important for operational design and applicable practice of the adsorption system (Chen X., 2015). Adsorption isotherm models are described in many mathematical forms, some of which are based on a simplified physical description of adsorption and desorption, while others are purely empirical intended to correlate experimental data. Adsorption equilibrium is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with interface concentration PiccinJ., Dotto G., Ointo L. 2011). A dsorption equilibrium is established when an adsorbate containing phase has been contracted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration (Ghiaci M., Abbaspur A., Kia R., and Seyedeyn-Azed F. 2004). Adsorption equilibrium is defined being a state of dynamic equilibrium, with both adsorption and desorption rates are equal (Langmuir I., 1916). The mathematical correlation constitutes an important role towards the modelling analysis, operational design and applicable practice of the adsorption systems, is usually depicted by graphically expressing the solid-phase against its residual concentration (Ncibi M., 2008). The physicochemical parameters together with the underlying thermodynamic assumptions of an isotherm provide insight into the adsorption mechanism, surface property and the degree of affinity of the adsorbents which are fundamentals in the characterization of adsorption process (Adejo S. and Ekwenchi M., 2014).

A wide variety of equilibrium isotherm models; Langmuir, Freundlich, Brunauer-Emmett-Teller, Redlich-Petrson, Dubinin- Radushkevich, Temkin, Toth, Kobel-Coorigan, Sips, Khan, Hill, Flory-Huggins and Radek-Prauntz isotherm, have been formulated in terms of three fundamental approaches (Malek., and Farooq S., 1996). Kinetic consideration is the first approach to be referred. Hereby, adsorption equilibrium is defined being a state of dynamic equilibrium, with both adsorption and desorption rates are equal. Whereas, thermodynamics, being a base of second approach, can provide a framework of deriving numerous forms of adsorption isotherm models, and potential theory, as the third approach, usually conveys the main idea in the generation of characteristic curve. However an interesting in the isotherm modelling is derivation in more than one approach, thus directing to the difference in the physical interpretation of the model parameters (Foo K. and Hameed B., 2009)

2.4.4.1 Langmuir adsorption isotherm

This describes quantitatively the formation of a monolyer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of MB dye between the solid and liquid phases. The Langmuir isotherm is valid for monolyer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption on to the surface and no transmigration of adsorbate in the plane of the surface. Based upon this assumption, Langmuir represented the following equation (Dada A., Olalekan A., Olatunya A. and DADA O., 2012):

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{Q_m K_L} \tag{2.1}$$

Where:

C_e = the concentration of adsorbate at equilibrium (mg/L)

Q_e = the amount of MB dye adsorbed per gram of adsorbent (mg/g)

Q_m = maximum capacity of monolayer coverage (mg/g)

K_L = Langmuir isotherm constant (L/mg)

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by the following equation:

$$R_L = \frac{1}{(1+K_L C_o)} \tag{2.2}$$

Where K_L is Langmuir's constant and Co is any adsorbate concentration at which the adsorption is carried out

The R_L value indicate the shape of the isotherm to be either unfavourable if ($R_L > 1$), linear if ($R_L =1$), favourable if ($0 < R_L < 1$), or irreversible if ($R_L = 0$) Shaibu S Adekola F., Adegoke H. and Ayanda O., 2014.

2.4.3.2 Freundlich model isotherm

The freundlich isotherm is an empirical equation used to describe hetrogenous systems. This model is defined by thefollowing equation:

$$Q_e = K_F Ce^{1/n} \tag{2.3}$$

The linear form of this equation can be written as

$$\ln Q_e = \frac{1}{n} lnC_e + ln\, K_F \tag{2.4}$$

Where, K_F and n are Freundlich constants. K_F is a rough indicator of the adsorption capacity of the sorbent and n giving an indication of the favourable way of the adsorption process. The magnitude of the exponent, 1/n, gives an indication of the adsorption favourability. If the value of 1/n is less than one this indicates a normal adsorption. If n is between one and ten, it indicates a favourable sorption process.

As the temperature increases, the constant K and n change to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface (Kamal H., 2014).

2.4.4.3 Temkin model isotherm

This isotherm contains a factor reflecting the adsorbent-adsorbet interactions and suggested that because of these interactions the heat of adsorption of all the molecules in the layer decrease linearly with the coverage. The model is given by the following equation (Abd EL-Latif M., Ibrahim A and EL-Kady M., 2010):

$$Q_e = BlnC_e + \ BlnA \tag{2.5}$$

Where B = RT/b, b is the Temkin constant related to heat of sorption (j/mol); A is the Temkin isotherm adsorption constant (L/g) related to adsorption capacity; R the gas constant (8.314 J/mol K) and T the absolute temperature ^{o}K.

2.4.5 Adsorption thermodynamics

Adsorption thermodynamic where determined using the thermodynamic equilibrium coefficients obtained at different temperatures and concentration in order to verify possible adsorption mechanisms. The adsorption characteristics of a material can be expressed in terms of thermodynamic parameter such as ΔG (Gibbs free energy change), which can be calculated by the following equation (Shahryari Z., Goharrizi A. and Azadi., 2010)

$$\Delta \mathrm{G} = \ -\mathrm{RTlnk_d} \tag{2.6}$$

Where K_d is the thermodynamic equilibrium constant (Lg^{-1})

According to thermodynamics, Gibbs free energy (ΔG) is the difference between the adsorption enthalpy (ΔH) and adsorption entropy (Δ S) multiplied by the temperature.

$$\ln K_d = \ -\frac{\Delta \mathrm{H}}{RT} + \ \frac{\Delta \mathrm{S}}{\mathrm{R}} \tag{2.7}$$

In this way, by applying this concept to the equation (4.1), ΔH and ΔS can be determined using the Vant'Hoff plot (Figure 4.14), according to the above equation (2.7)

2.4.6 Adsorption kinetics

The study of the adsorption kinetics is important because it provides valuable insights in to the reaction path and the mechanism of the reactions. The adsorption rate was followed by the study of the contact time up to six hours and compared to theoretical models. Pseudo first-order, second-order kinetic models and intra-diffusion model were tested in this study where experimental date obtained for the different contact times were used.

The rate constant for the adsorption of adsorbate from the effluent on adsorbent is determined using Pseudo first-order equation (Lagergren equation): (Joseph J. and Xavier N., 2013)

$$\log(Q_e - Q_t) = Q_e - \left(\frac{K_1}{2.303}\right)t \qquad (2.8)$$

Where Q_e is the adsorption capacity of the adsorbent at equilibrium (mg/g), Q_t is the amount of dye adsorbed at a time t (mg/g) and K_1 is the pseudo first order rate constant (min^{-1}).

The pseudo second order kinitcs can be expressed in a linear form as integrated second order rate low.

$$\frac{t}{Q_t} = \frac{1}{Q_e}t + \frac{1}{K_2 Q_e^2} \qquad (2.9)$$

Where K_2 is the pseudo second order rate constant ($g\ mg^{-1}min^{-1}$).

A pseudo second order suggests that this adsorption depends on the adsorbate and the adsorbent and involves chemisorptions process in addition to physisorption. The chemisorptions might be the rate limiting step where valance forces are involved via electrons sharing or exchange between the adsorbent and the adsorbate (Kamal H., 2014)

Intra-particle diffusion can be described by three consecutive steps

1. The transport of sorbate from bulk solution to outer surface of the sorbent by molecular diffusion, known as external (or) film diffusion.

2. Internal diffusion, the transport of sorbate from the particles surface into interior sites.

3. The sorption of the solute particles from the active sites into the interior surface of the pores.

The overall rate of the sorption process will be controlled by the slowest, the rate limiting step. The nature of the rate-limiting step in a batch system can be determined from the properties of the solute and sorbent. In adsorption systems where there is the possibility of intra-particle diffusion being the rate-limiting step, the intra-particle diffusion approach described by Weber and Morris. The rate constants, for intra-particle diffusion (k_{id}) are determined using equation given by Weber and Morris.

$$q_t = K_{id} * t^{0.5} \tag{2.10}$$

Where qt is the amount of dye adsorbed, t is the contact time; k_{id} is the intra-particle diffusion coefficient and c is constant.

A plot of qt against $t^{0.5}$ should give a straight line which pass through the origin for intra-particle diffusion controlled adsorption process. The value of k_{id} can be calculated from slope of such plot. The values of the constant illustrate the effect of boundary layer on the rate of adsorption.

2.4.7 Types of adsorbents

Different types of adsorbents are classified in to natural adsorbents and synthetic adsorbents. Natural adsorbents include charcoal, clays, clay minerals, zeolites, and ores. These natural materials, in many instances are relatively cheap, abundant in supply and have significant potential for modification and ultimately enhancement of their adsorption capabilities. Synthetic absorbents are adsorbents prepared from agricultural products and wastes, house hold wastes, industrial wastes, sewage sludge and polymeric adsorbents. Each adsorbent has its own characteristics such as porosity, pore structure and nature of its adsorbing surfaces. Many waste materials used include fruit wastes, coconut shell, scrap tire, bark and other tannin-rich materials, sawdust, rice husk, petroleum wastes, fertilizer wastes, fly ash, sugar industry wastes blast furnace slag, chitosan and seafood processing wastes, seaweed and algae, peat moss, clays, red mud, zeolites, sediment and soil, ore minerals etc (Rashed N., 2013).

2.4.8 Adsorption as an effective method for removing dyes from wastewater

Many treatment methods have been used to remove the dyes from wastewater. These can be divided in to physical, chemical, and biological methods. Among the various methods, adsorption is an effective separation process for a wide variety of applications. It is now recognized as an effective and economical method for the removal of both organic and inorganic pollutants from wastewater. Adsorption is a common technique used for dye removal from aqueous solution, mainly because it is starting point in the development of an adsorption unit is the choice of an adsorbent among the various adsorbents.

Due to law biodegradation of dyes, a conventional biological treatment process is not very effective in treating a dyes wastewater. It is usually treated with either by physical or chemical processes. However, these processes are very costly and cannot effectively be used to treat the wide range. The adsorption process is one of the effective in treating a dyes wastewater. The adsorption process is one of the effective methods for the removal dyes from the waste swage. The process of adsorption has an advantage over the other methods due to its sludge free clean operation and completely removed dyes, even from the diluted solution48. A synthetic dye in wastewater cannot be efficiently decolorized by traditional methods. This is because of the high cost and disposal problems for treating dye wastewater at large scale industries. Adsorption is a well-known equilibrium separation process for water decontamination applications. Adsorption has been found to be superior to other techniques for water reuse in terms of initial cost, flexibility and simplicity of design and ease of operation. (Dargo H., Gabbiye N. and Ayalew 2014).

Adsorption is a fundamental in the physicochemical treatment of municipal wastewater, a treatment which can economically meet today’s higher effluent standards and water reuse requirements. Adsorption is integral to a broad spectrum of physical, biological and chemical processes and operations in the environmental field. Purification of gases by adsorption has played the major role in air pollution control, and adsorption of dissolved impurities from solution has been widely employed for water purification. Adsorption is now viewed as a superior method for waste water treatment and water reclamation. Applications of adsorption chemical processing air pollution control and water treatment are well known, applications in wastewater treatment and water pollution control are generally not as well recognized, nor as well understood. The process has been demonstrated to be widely effective for removing dissolved organic substances from wastewaters, but it should not be viewed as a catholicon for waste treatment, nor should its application be made in an empirical fashion (Ruthven D.M and John Wiley 1984).

MB is a basic dye & got many utilities in terms of dyeing of silk, leather, paper & cotton as well as production of ink. The discharge of MB is a great threat for both toxicological & aesthetical reasons impede light penetration & are toxic to supply food chain for organisms.

Since it has a synthetic origin & complex organic aromatic structure; hence, they are inert & difficult to bio-degrade when discharged into the water. The various treatment options have been explored and adsorption technique has been widely welcomed for the removal of methylene blue dye from the effluent using silica gel as adsorbent.

Syntheses of silica gel since 1992 have been commonly used as adsorbents (Paul et al. 2012). They are of interest because of their relatively large pores, which facilitate mass transfer, the very high surface area, which allows a high concentration of active sites per mass of dye and high mechanical stability. In addition, it is possible to change their surface chemistry by anchoring various chemical functional groups onto pore walls, which are exceptionally selective and have a high capacity for adsorbing various dyes. The three consecutive steps in the adsorption of dye by MPSs adsorbent are:

I. Transport of the dye to the external surface of the adsorbent (film diffusion).
II. Transport of the dye within pores of the adsorbent, only a small amount of the dye is adsorbed on the external surface (particle diffusion).
III. Adsorption of the dye on an inner surface of the adsorbent.

2.5 Silica gel production

2.5.1 Silica

Silica is one of the most abundant and most complex materials, existing no matter as being synthetically produced or natural materials, f or example fumed silica, fused quartz, crystal, amorphous, silica gel and silica sol. Colloidal silica is suspension solution, which contains spherical and amorphous silica particles. Uniform particle size of colloidal silica is approximately from 5 nm to 1500 nm , typically from 5 nm to 100 nm (Horacio E. Bergna, William O. Roberts. 2006.)

2.5.2 Properties of silica

Silica can be assumed a polymer of silicic acid, which contains cross-linked SiO_4 units, so that molecular formula of silica is SiO_2. As can be seen in Figure 2.5.2, two molecules of silica shared one oxygen atom. Si - O- Si bond angle is displayed in figure 2.3 (Kingery, W. D., Bowen, H. K., Uhlmann, D. R. 1976). Moreover, the density of colloidal silica particles is between2.1 to 2.3 g/cm3. Silica is in different forms in nature, such as sand, quartz and glass etc. Colloidal silica is the form of colloidal state of silica particles in liquid phase. In colloidal silica, silica particles will be linked together in both small size (1 nm) and sufficiently large size (1 mm). No matter what kind of the size, surface forces and Vander Waals attraction are the most common interaction forces between molecules.

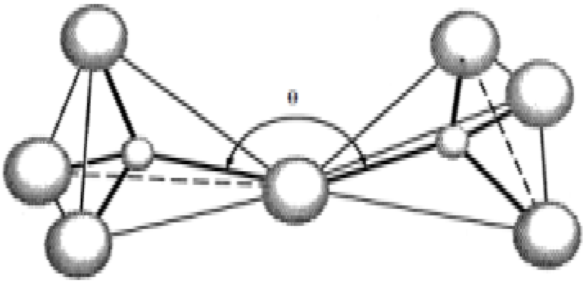


Figure 2. 2: Schematic representation of adjacent SiO4 tetrahedral that shows the Si - O- Si bond angle, small circle, Si, large circle, ( ] Kingery, W. D., Bowen, H. K., Uhlmann, D. R.).

2.5.3 Stability of colloidal silica

Colloidal stability is very important parameter when applying colloidal silica, no matter in mechanical, chemical or thermal area. Stability in colloidal state means that colloidal particles do not settle in short time or bunch up to form larger cluster and then settle after a short period (Everett, D. H. 1971). In this case, colloidal silica is easy to link together with other particles by aggregation , coagulation, flocculation, gelation etc. If particles link together to form larger clusters or three dimensional networks and start to settle down in liquid phase, even become gel form, it means that silica sols have lost their stability.

Even though both gelation and coagulation will make silica sols lose their stability, they are basically different with each other. When a sol is gelling, colloidal silica particles link with each other one by one and form long chains. As a result, sol will become more viscous and finally look like soft solid materials. On the other side, coagulation somehow means that precipitation. Silica particles will link with each other and form clusters. When clusters become large enough, they will settle down, so that sediments in the liquid phase can be seen at the bottom of containers. Figure 2.4 (Iler, R. K. 1979) Shows the difference between a sol, gel and precipitate of silica.

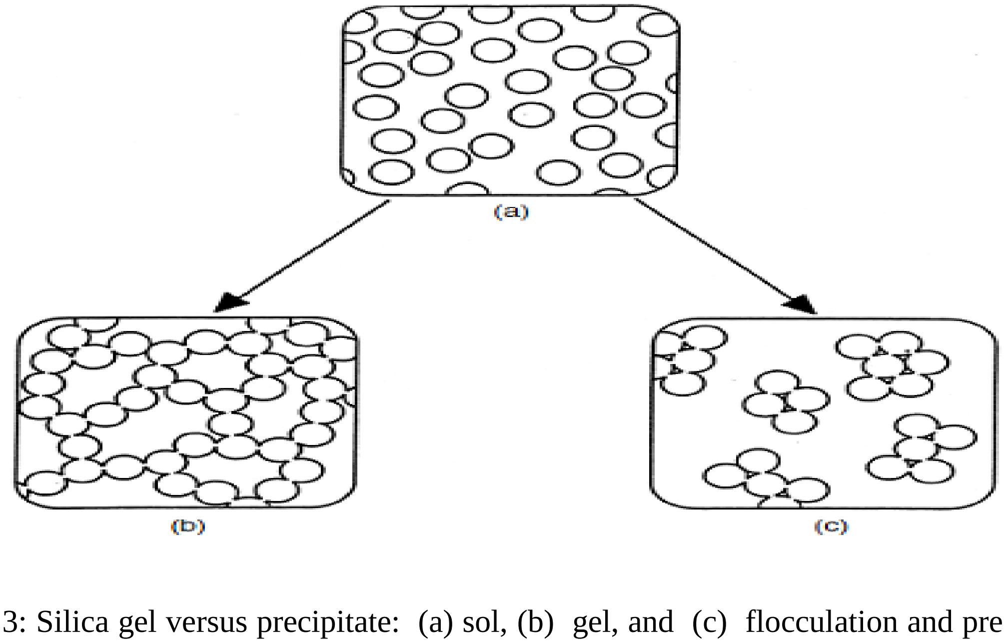


Figure 2. 3: Silica gel versus precipitate: (a) sol, (b) gel, and (c) flocculation and precipitation (Iler, R. K. 1979)

2.5.4 Method of synthesis of silica gel

Silica gel is an adsorbent prepared from the coagulation of colloidal solution of silicic acid. There are several methods to synthesize silica gels. Tetraethyl orthosilicate (TEOS) is one of the most common raw materials on silica production. Actually, sodium silicate as another kind of silica raw materials, has many benefits, such as a slow grow rate, low cost, possibility of particle surface modification etc. Most commonly silica gels are manufactured by acidifying an aqueous solution of sodium silicate. The material that 1st form is called a hydrosol, the particles of which agglomerate and results in the growth of silica polymers. The hydrosol is typically formed at low pH and if the subsequent washing steps are also conducted at relatively low pH, the final product then has high surface area (> 700 m^2/g). When hydrosol ceases to flow like a liquid (the gel time), it is termed as hydro gel.

Interaction of acid with sodium silicate solution produces orthosilicic acid which is an intermediate product of the hydrolysis. It is very unstable substance which readily condenses with itself to give a colloidal polymer of silica sol.

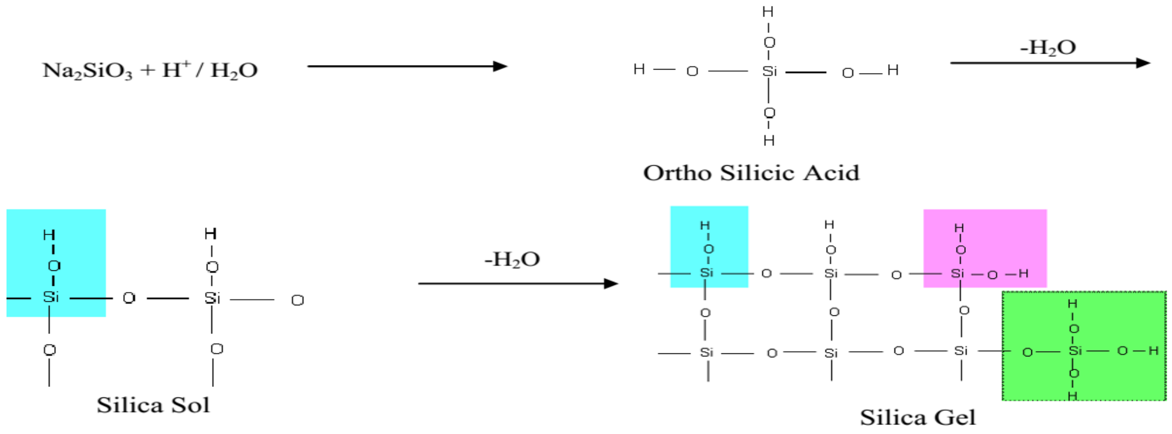


Figure 2. 4: Different forms of hydroxyl group that can occur on the surface of Silica Gel.

Further condensation of silica sol takes place on standing which assumes the form of a gel. Silica gel is a continuous three dimensional network of spherical particles of colloidal silica. Both siloxane (-Si-O-Si-) and silanol (-Si-OH) bonds are present in the gel structure. The pores of the gels are interconnected and filled with water from hydrolysis and condensation reaction.

The silanol groups in turn may condense to form siloxane bridges (-Si-O-Si-). Therefore, the surface composition of silica gel Fig. 2.5.4b is made up of physically adsorbed water, chemically bound water and silicon dioxide (J. Bouaziz, B. Elleuch, R. Garbi, J. Soc. Chim. de Tunisie 3).

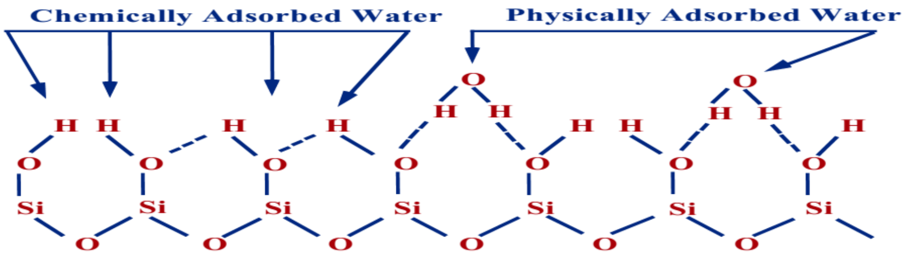


Figure 2. 5: Silica gel surface showing physically and chemically adsorbed water

The rate of gelation of silica sol is greatly influenced by the amount of water present, the pH of the sol and the temperature of the contents. The characteristic of silica gel is to shrink on standing during which process known as syneresis, a liquid phase (water) is squeezed out of the gelly. Further removal of water by evaporation produces different grades of silica gel depending upon the number of hydroxyl groups left or removed after dehydration. A typical good quality adsorbent silica gel has a residual water contents of about 6 %, is hydrophilic and has a surface area of 200-800 m2/gm (E. Ellaloui, G.M. Pajonk, J. Soc. Chim. de Tunisie 4 (2000))

. Silica gels may be examined/analyzed for various applications by determination of their adsorption isotherms. Bulking value, decolourization, dry gas capacity, equilibrium capacity, gas adsorbent tests, hardness, heat of adsorption, heat of wetting, iodine adsorption, retentivity value, water contents, water soluble matter, moisture absorptive capacity and heat resistance are some of the tests carried out on silica gels (T. Woignier).

2.5.5 Silica gel manufacturing method

The method of producing silica gel is said to be efficient and costly when a silica gel material is produced through a process that

- does not require a first step of forming a semi-solid gel of low solids content, but actually entails a first step of producing gel materials in liquid phase form.

- the precursor material is cheap and easily available.
- required much shorter aging times to provide a proper solid material.
- has the ability to avoid introduction of ammoniacal solvents.
- has the ability to exhibits the similar pore sizes as previously required of long aging times through pH modifications instead.
- relative require ease in salt removal provided with lower amounts of needed water for such a process step.
- provides a soft gel material with large pore sizes upon incorporation of proper high pH caustic during the manufacturing thereof.

So the efficient method of producing silica gel material consists of the following sequential process steps.

a) initially producing a silicic acid sol through alkali metal silicate addition to a mineral acid, wherein the reaction occurs at a target pH level of between 3 and 4.5;
b) quenching silicic acid sol in a hot water medium at a temperature of from about 65 to about 100° C to solidify the sol into a polysilicic acid gel;
c) aging the resultant gel of step "b" in salt water;
d) washing aged gel of step "c" to remove excess salt; and
e) drying washed gel of step "d" to form a dry silica gel.

Such a process avoids silica gelation in the reactor, instead gelling the silica in the filter feed tank, thus enabling the gel to be made using common precipitation reactors. The transfer of the polysilicic acid solution into the filter feed tank can be varied, either through the utilization of pumps or reliance on gravity. The term "sol" is intended to encompass any suspension of fine silica particles in an aqueous media. The term "gel" is intended to encompass a three-dimensional network formed by silica particles, in either wet or dry form due to the reaction of sodium silicate and sulfuric acid. The resulting gel from this process usually remains acidic ($pH<=6.5$) and such a resultant gel exhibits excellent properties for certain filter media applications, among other end uses. Additionally, though a pH adjustment can be performed in step (b), to create a higher pH gel through caustic introduction during step (b), by subsequently controlling the pH of the final pH in step (c), a caustic gel (pH>7) with larger pore volume capacity and larger pore diameter can be produced as a result. If an alkali metal hydroxide is utilized as the caustic material (such as sodium hydroxide), the high solubility of the sodium species within the reaction medium creates a caustic environment in which the sodium cation washes from the gel during such a step. The introduction of a high pH caustic enables pore size, pore diameter, etc., modifications within the produced gel in order to avoid aging steps of long duration with high temperatures, thereby permitting a much quicker and more efficient manner of tuning the ultimate gel materials' physical properties; the ability to impart other properties in terms of caustic and/or composite structures is an unexpected added benefit of such an efficient gel production method. Thus, the pore volume and diameter are surprisingly tunable with differing levels of added caustic introduced within this second step, contrary to the past possibilities available from typical and traditional gel production processes. In comparison with acidic gel wet cakes, improved washing efficiency of the caustic gel wet cake is observed. Through the utilization of a vacuum filter and the same amount of water, caustic wet gel cakes can be washed with less than half of the time as compared to the acidic wet gel cake, and exhibits a lower final salt content. The basic silica gel should be beneficial as neutralizing high capacity absorbents for (acidic) contaminants encountered.

Typically, silica gel is prepared by mixing an aqueous alkali metal silicate solution, usually sodium silicate, and an aqueous mineral acid solution, usually sulfuric acid, to form a silica hydrosol and allowing the hydrosol to set to a hydrogel. The weight ratio of SiO_2 to Na_2O of from about 1:1 to about 1:3.4. The reaction is generally carried out at temperatures of from about 15 to about 80° C. and typically is carried out at an ambient temperature (i.e., from about 20 to 25° C. at about 1 atmosphere pressure).

When the quantity of acid reacted with the silicate is such that the final pH of the reaction mixture is acidic, typically from about 1 to 5, the resulting product is considered an acid-set hydrogel. The hydrogel granules are then washed with water or acidified water to remove residual alkali metal salts which are formed in the reaction. Acidified water is preferred and usually has a pH of from about 1.0 to about 5.0, preferably from about 2.5 to about 4.5. The acid may be a mineral acid such as sulfuric acid, hydrochloric acid, nitric acid, or phosphoric acid or a weaker acid such as formic acid, acetic acid, oxalic acid, citric acid, tartric acid, nitriloacetic acid, ethylene diamine-tetraacetic acid, or propionic acid. The water usually has a temperature of from about 80 to about 200° F. (27-93 °C.), preferably about 90 °C.

The resulting gel in the filter feed tank is aged for a time of from 0.5 to 4 hours, at a temperature of from 65 to 100 °C., and, depending on the resultant silica gel desired, at a pH level of either acidic (less than 6.5) or basic (above 7.0). After aging, the resultant gel is then reslurried and filtered via a press filter for washing and filtering. The pressed cake can be dried by any conventional means such as oven drying, tray drying, flash drying, or spray drying and ground in a fluid energy mill, hammer mill, or other known mill to the desired particle size. Generally, the ground gels have a weight median particle diameter of from about 1 to about 40 microns.

Silica gels made by this process typically will have BET surface areas of 350-1000 m_2/g with pore diameter of 17 Å-45 Å. As for the caustic gels, the pore sizes ranged from about 60 to 200 Å (Duen-Wu Hua, Michael C. Withiam, Francis R. W. Godwin, Fitzgerald A. and Sinclair., 2010)

2.5.6 Factors and additives that have effect of synthesis of silica gel

There are many factors that have great effect on synthesis of silica particle, such as silica surface area, particle size of produced silica, reaction rate. Effect of pH, silica source concentration, acid, salt concentration will be further discussed as follows.

2.5.6.1 Effect of pH of silicic acid sol

The pH has great effect on not only porosity but also particle size of silica particles. Tzong – HorngLiou found that pH strongly affect the surface area of silica particles. Surface area decreases with increasing of pH value, i.e. the silica obtained at pH 9 had the lowest surface area (237 m^2/g), while the highest surface area (634 m^2/g) was obtained at pH 3. When pH increases from 3 to 9, as shown in the following two paths, a condensation reaction may happen during gel formation, resulting in increasing particle size and porosity.

$$\mathbf{OH)_3Si - OH + OH \longrightarrow (OH)_3Si - O\text{-}+ H_2O} \qquad (2.10)$$

$$\mathbf{(OH)_3Si - OH + (OH)_3Si - O^- \longrightarrow (OH)_3Si\text{-}O\text{-} Si(OH)_3 + OH} \qquad (2.11)$$

Where, the OH plays an important catalyst role. In the acid regime, reduced pH leads to changing of siloxane bonding (Si - O- Si) to silanol bonding (Si - OH) and gel formation is slow.

As can be seen above, the OH increases the reaction of equation (2.10). In the acid solution, decreasing of OH will result in more siloxane linkages (Si - O- Si) change into silanol groups (Si - OH), so that colloidal suspension becomes more stable. In the basic solution, reaction will reverse so silanol groups will change into siloxane In this case, silica is composed of small particles and therefore, possesses high surface area. In the basic regime, surface silanol bonding tend to form siloxane bonding. Siloxane linkages create negative charges and increased electrostatic repulsion between silica particles (J. Schlomach and M. Kind, J. 2004).

The charge develops silica particles to connect together more, so that particle size becomes larger when pH increases. That is why higher porosity and lower surface area will be obtained in this situation.

2.5.6.2 Effect of salt concentration

The dehydration reaction of silicic acid will happen in the alkali solution (Horacio E. Bergna, William and O. Roberts. 2006.). In this case, silica form nuclei first and thus particle grows further. Therefore, increasing salt concentration means increasing sodium ion concentration, resulting in larger particle size of produced silica.

Furthermore, other parameters would have an effect on the formation of colloidal silica, such as SiO_2:Na_2O ratio, the titration rate, reaction time, stirring speed. In order to get the most desired silica sol, experiment should be taken under optimum condition. In my study, the easiest method of synthesis under mild conditions and common raw materials were used for industrial application in the future. Titration of sodium silicate and sulfuric acid simultaneously to water vessel with 200 rpm stirring speed and desired temperature, while keeping pH of vessel constantly.

The flow diagrm for production of silica gel is presented in Figure 2.5

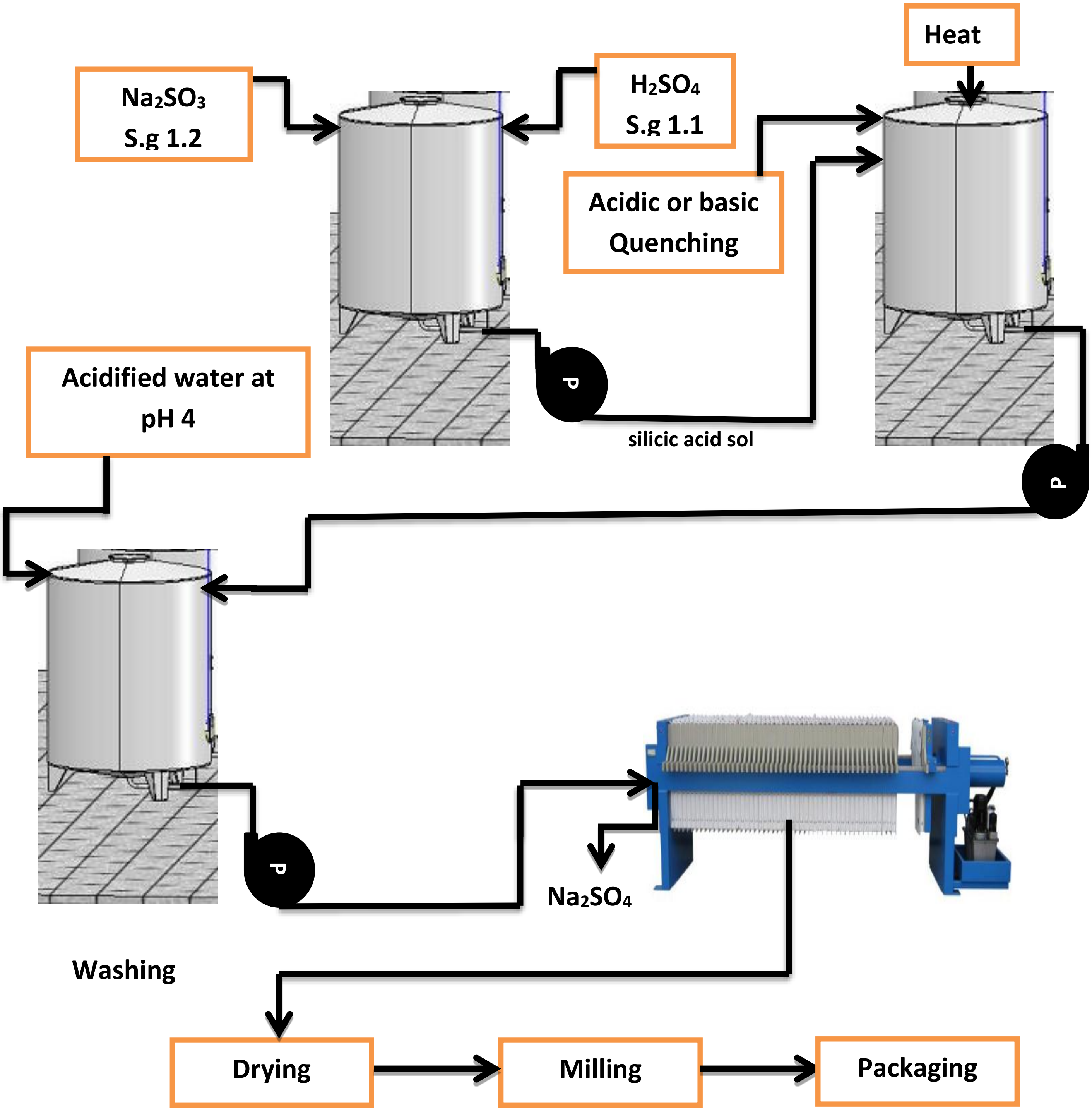


Figure 2. 6: Flow diagram for production of silica gel

3. MATERIALS AND METHODS

3.1 Chemicals and instrumentation

3.1.1Chemicals

Commercially available liquid Sodium silicate (sp. gr. 1.43) (SiO_2:Na_2O=2.5-2.7) elide chemicals p.l.c Ethiopia, with measured solid content of 43%, analytical grade concentrated Sulphuric Acid (95- 97%, Merck) with (sp. gr. 1.84) and analytical grade NaOH was used for experiments to prepare silica gel.

Methylene blue dye, chemical formula, $C_{16}H_{18}N_3ClS$ and molecular weight of 319.5 was used for the initial adsorption experiments. Other chemicals such as NaOH and H_2SO_4 were used for preparing solutions of varying pH.

3.1.2 Instrumentation

A hydrometer was used to adjust the specific gravity of Sodium silicate and sulphuric acid. A water bath was used for maintaining the desired temperature. An oven is used for drying the wet cake gel. XRD analysis was carried out to know the produced product is amorphous or crystal and to verify the by-product NaSO4 formed during the reaction is completely removed or not. FTIR analysis was also carried to know what bonds are present in the prepared silica gel and to identify the purity of amorphous SiO_2.

A shaker was used for all the adsorption experiments. A UV-ray spectrophotometer was used to determine the absorbance. The pH meter was used to measure the pH of solution. Glass wares & conical flask were used to handle the solutions. A meter balance was used to weigh the samples. Pipette was taken in transferring the solution into the test tube to record the absorbance of solution.

3.2 Method of synthesis of silica gel

3.2.1 Preparation of raw materials

Concentrated sulphuric acid and sodium silicate were diluted with distilled water to get the required specific gravities. The solutions of sodium silicate and sulphuric acid of specific gravities 1.20 &1.10 were prepared with the help of "Hydrometer".

3.2.2 Procedure for synthesis of silica gel

Silica gel production consists the following method steps:

1. A silicic acid sol was made by adding Sodium silicate of known specific gravity slowly into the beaker containing Sulphuric Acid (75 gm) of known specific gravity to a target pH values of between 3 and 4.5 to form a quasi-stable sol under sufficient agitation to stir with minimal splashing (˜120 RPM), the RPM was raised to 250 and gradually increase to 300 over a period of several minutes. pH control in this stage is critical as it is this reaction pH that dictates the pore size distribution in the final product. The addition of sodium silicate solution into sulphuric acid will be completed between time intervals of 18 to 20 minutes. The reaction was carried out at room temperature.

2. Hot water medium was prepared by introducing 1 litre of water into a 3 liter beaker. The pH thereof was adjusted to about 4 with H_2SO_4 and 9 with diluted NaOH the formulation was then heated to 90° C using a water bath.

3. The sol was then quenched in a prepared hot acidified and basic water medium for 3 hours to solidify the silicic acid sol into the more stable polysilicic acid gel.
The hot water medium essentially provides the multiple functions of

a) Speeding up the gel process as a result of the increased temperature,
b) Diluting the salt present in the sol thereby requiring less washing,
c) Having the gel form into discrete individual agglomerates which allowed for the migration of salt across a shorter distance thereby speeding up wash time;

4. The gel then Aged for 12 hour at room temperature.
5. The sodium sulphate formed during the reaction will be removed by washing the hydro gel by

2.5 liter hot acidified water of pH 4 for six hour with periodical agitation. The temperature was then maintained at about 90° C.

6. The resultant gel slurry was then vacuum filtered by using filter paper to rid the excess salt. The washing of the hydro gel is necessary in order to get good quality product and optimum yield. If the washing was not done, the product becomes powder on drying

7. Drying will be carried out in order to remove the adhered water from the gel. After washing, the prepared samples of silica gels will be placed in an oven at 110ºC then left it for overnight stay. The heating time will be prolonged till constant weight was obtained. On drying, the product automatically disintegrated into transparent crystals of various sizes depending on the experimental conditions.

9. Optionally the dried gel was milled.

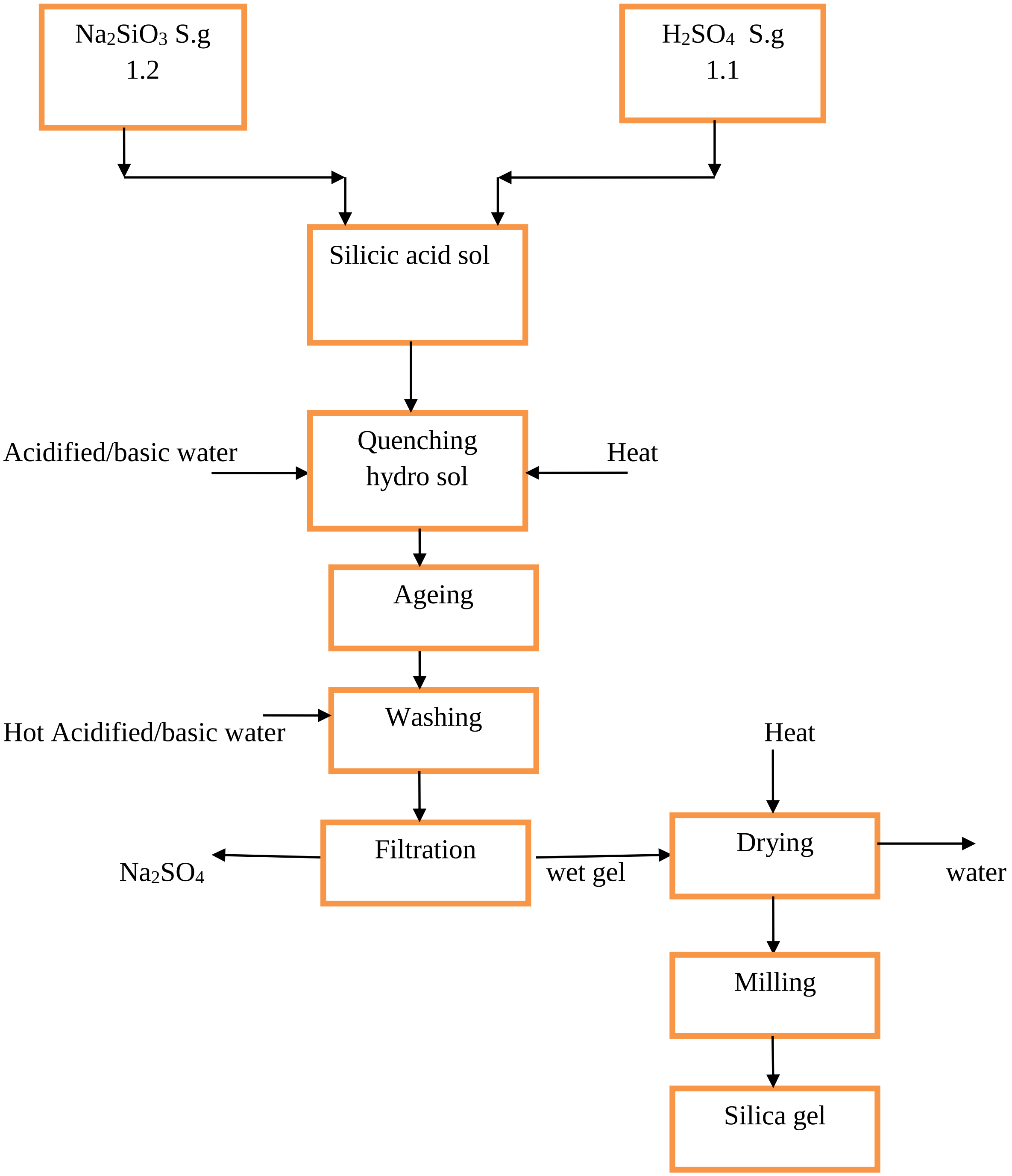


Figure 3.1: Block diagram of silica gel production

3.2.3 Determination of optimal conditions for Silica gel production

Specific surface area (S) of an adsorbent is a significant characteristic: it is the surface offered by the pores of one gram of solid (m^2/g). It is the sum of external and internal surfaces, i.e. the geometrical surface of the particles and the surface developed by the walls of the pores.

The Design expert 7.0.0 software was followed to determine the optimal conditions of silica gel production from Ethiopia sand using sol-gel method to adsorb MB dye. Among the variables that influence the final properties of silica gel major two variables are selected. Those are final PH of the silicic acid sol and pH of quenching water and the response is MB dye adsorption capacity of silica gel (Qe) mg/g. According to designee expert 7.0.0 the final number of experiments will be 16 with one repetition.

Table 3. 1: variables that highly influences the adsorption capacity of silica gel

pH of quenching water	pH of silicic acid sol			
4	3	3.5	4	4.5
9				

3.3 Method of characterization of silica gel

The prepared silica gel was characterized using FTIR and XRD analysis. The caustic and acidic silica gels were characterized by X-ray diffraction (XRD, X'pert PRO PANalytical) using CuKα radiation (0.154060) source operated at 40 kV and 40 mA. XRD analysis was carried out to know the produced product is amorphous or crystal and to verify the by-product $NaSO_4$ formed during the reaction is completely removed or not. The diffraction patterns were obtained in the 2θ range from 10-80°. Fourier transform infrared (FTIR, Buck Scientific 500), in the wave number range of 4000-400 cm^{-1} to identify types of bonds present in the particles.

3.4 Preparation of methylene blue solution

About 1g of methylene blue was taken in a 1000 mL volumetric flask and diluted up to the mark by addition of deionized water. Different concentration; 5, 10, 15, 20, 25, 30, 40 and 50 mg/L were prepared by dilution (Wong Y., Senan M. and Atiqah N., 2013).

3.5 Preparation Calibration curve

A standard calibration curve was prepared by measuring the absorbance by UV-visible spectrophotometer at 665 nm of different concentration of diluted MB solution of 5, 10, 15, 20, 25, 30, 40 and 50 mg/L. At high concentrations of MB dye, Beer-Lambert relation deviates from linearity and give a non-linear relationship, as shown in Figure 2.8, so our work was restricted at concentrations up to 25 mg/L. at higher concentrations, the individual particles of analyte will not behave independently of each other. This interaction between the particles resulting from the analyte can change the value of molar absorptivity (ε). Also absorption capacity (a) and molar absorptivity (ε) are depend on the sample refractive index. Since the refractive index varies with the concentration of the analyte, the values of “a” and “ε” also changes. At enough low concentration of analyte, the refractive index remains constant, and the calibration curve is linear Umoren S., Etim U. and Iserael A. 2013). Few large ions or molecules deviate from Beer-Lambert law even at low concentration of the analyte, for example, MB dye which has absorbance at 436 nm fails to obey Beer-Lambert law even at concentrations as low as 10 µM (Mahta A., 2012). Linear calibration curve between the absorbance and the concentration was obtained with MB concentrations in the range 5- 15 mg/L ($R^2 = 0.9961$) as shown in Figure 3.2 (b).

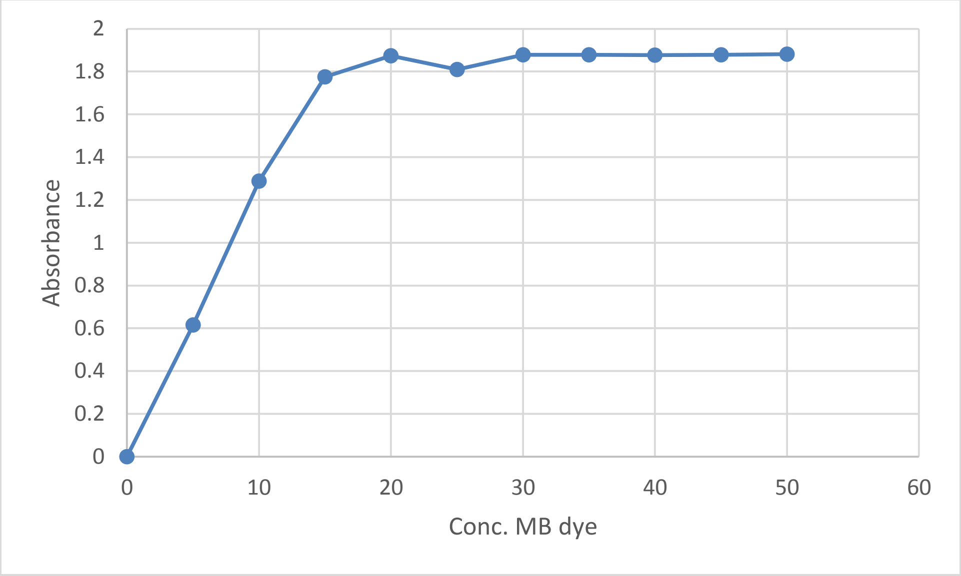


Figure 3.2: (a) A representative plot of the absorbance versuse concentration of MB dye

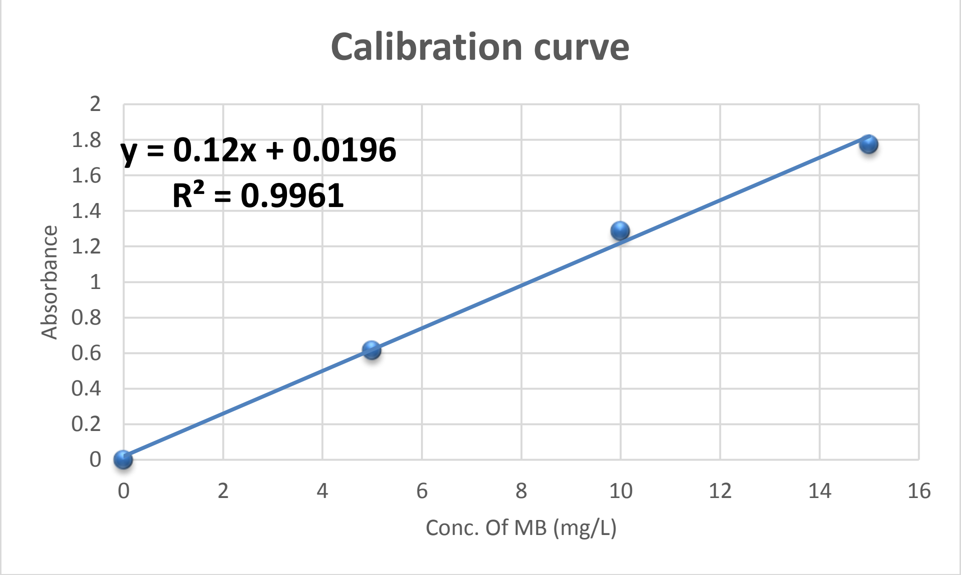


Figure 3.2: (b) Linear calibration curve of absorbance vs. concentration of MB dye concentrations in the range 5-15 mg/L

3.6 Adsorption experiments

The maximum absorbance (λ_{max} = 665) was used for measuring the absorbance of residual concentration of MB. The pH of solution was adjusted using roughly concentrations of 0.1M H_2SO_4 and 0.1M NaOH. By studying batch mode experimental studies the efficiency of the adsorbent was evaluated. The adsorption behaviour of silica gel with MB dye was studied. The effect of pH, temperature, dose of adsorbent, concentration of MB solution and the contact time on adsorption of MB dye was studied. The adsorption capacity was investigated using kinetics and pH effect. Equilibrium isotherm studies were conducted by varying the following parameters: initial concentration of MB dye solution, temperature, and adsorbent dose on dye adsorption from the solution. At the end of time terms, the adsorbent was removed by a centrifuging at 600 rpm and supernatant was analyzed by UV-visible spectrophotometer for the residual concentration of MB, at 665 nm wavelength.

The proportion of dye removal (% removal) is recognized as the ratio disparity of the dye concentration before and after adsorption to the initial concentration of dye in the aqueous solution and was calculated by the following equation (Visa M., BOgatu C., and Duta A 2010):

$$Removal\ efficency\ (\%) = \left[\frac{C_0 - C_e}{C_0}\right] \times 100 \tag{3.1}$$

Where, C_0 is the initial dye concentration (mg/L) in the sample and C_e is the final dye concentration in the sample solution after treatment.

In this study, the data were fitted using Langmuir and Freundlich and Temkin models. Each of these models makes use of a parameter qe (i.e. adsorption capacity per unit mass of the adsorbent at equilibrium in mg/g.

$$q_e = \frac{(C_o - C_e) \times V}{m_{ads}} \tag{3.2}$$

Where C_0 = Initial concentration of solution (mg/l)

Ce = Equilibrium concentration of solution in (mg/l)

V = Volume of solution in litre

m_{ads}= mass of adsorbent used in g

3.6.1 Experiment 1The temperature effect

For studying the temperature effect on adsorption, 50 mg adsorbent sample were added to 50 ml of methylene blue dye solutions with concentration 20 mg/L at pH 10.01. Each mixture was placed in a shaker at desired temperature (the range was 29.5 – 55 ^{o}C) for 30 min (Daqihan Labtech). At the end of each time interval, the adsorbent was separated by by a centrifuging at 10000 rpm and supernatant was analyzed by UV-visible spectrophotometer for the residual concentration of MB, at 665 nm wavelength.

3.6.2 Experiment 2 Effect of pH

Effect of pH on adsorption was investigated in the pH range 2.5 - 12. The pH was adjusted using roughly concentration concentrations of 0.1M HCL and 0.1M NaOH. 50 mg adsorbent sample were added to 50 ml of methylene blue dye solutions with concentration 20 mg/L. Each mixture was placed in a shaker at temperature of 25 ^{o}C for 1hour. At the end of time interval, the adsorbent was separated by by a centrifuging at10000 rpm and supernatant was analyzed by UV-visible spectrophotometer for the residual concentration of MB, at 665 nm wavelength.

3.6.3 Experiment 3 Effect of initial concentration of MB dye

In order to find out the optimum concentration, 20 mg of adsorbent was added to a number of conical flasks contains 50 ml of different concentrations of MB dye solution (5-25 mg/L), under optimized temperature 25 ^{o}C and pH 10.04 for 15 min. The absorbance of the solution above the solid residue was measured by UV-visible spectrophotometer.

3.6.4 Experiment 4 Effect of adsorbent dose

The effect of adsorbent dose on the adsorption of MB dye system was studied. In order to find out the optimum adsorbent dose, 0.005g,0.01g,0.015g and 0.2g were added to four vials contains 50 ml of 20mg/L MB dye solution at pH 10. The mixtures were placed in a shaker at temperature 25 ^{o}C for 1 hour. The absorbance of the solution above the solid residue was measured by UV-visible spectrophotometer.

3.6.5 Experiment 4 Optimizing of contact time

The adsorption of MB on the adsorbent was studied as a function of shaking time at 20 ^{0}C. A sample of 50 ml of dye (20 mg/L) at pH 10.06 was taken in a volumetric flask and shaken with 0.02g of adsorbent for 20, 30, 45, 60, 75, 90, 105, 210 and 360 min. At the end of each time interval, the adsorbent was separated by by a centrifuging at 10000 rpm and supernatant was analyzed by UV-visible spectrophotometer for the residual concentration of MB, at 665 nm wavelength.

3.6.6 Experiment 5 Effect of particle size of silica gel

Three different sized particles of ≥ 250 µm, 250 µm ≤ 150 µm, 150 µm ≤ 100 µm and 100 µm ≤ 63 µm were used in 20 mg/L dye concentration. Contact time, adsorbent dose, volume temperature and pH of 60 minutes, 0.02 mg, 50 ml, 25 ^{O}C and 7 respectively were kept constant.

3.7 Thermodynamics and kinetics of adsorption

The removal of MB dye was studied by adsorption technique using the prepared adsorbent (silica gel). The method was arranged under the optimized case of adsorbent dose, contact time, concentration, temperature and pH. Using UV-visible spectrophotometer, the concentration of dye was determined before and after adsorption. The data was provided in to Langmuir, Freundlich and Temkin adsorption isotherm equation. The values of their relevant parameters were determined. Thermodynamic parameters like Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of the systems were calculated by using Van't Hoff's plot. Removal proportions and K_d values for dye systems were calculated at different temperatures between (29.5 - 55 ^{0}C).

0.02g of adsorbent was added to 50 mL of 20 mg/L of MB dye solution at pH 10. The mixture was placed in a shaker at constant temperature (25 ^{0}C). The rate of adsorption was observed by studying the contact time up to 6 hours and matched to theoretical models. Pseudo firs-order, second-order kinetics and intra-particle diffusion models were examined in this study using experimental data obtained for different periods of contact time, parameters of Pseudo firs-order and second-order kinetics models, (K, Q_e and R^2) and Temkin parametrs (b, A and R^2) were determined. The values of the calculated and experimental Q_e were compared.

4. RESULT AND DISCUSSION

4.1 synthesis of silica gel

In the present studies non indicating (white) amorphous silica gels were prepared from solution of sodium silicate and sulphuric acid. Silica gels were prepared with at different pH level of the hydro sol and at different pH of quenching water. The Physical properties of the prepared silica gel samples are presented in Table 4.1.

Table 4.1: The Physical properties of the prepared silica gel samples obtained, by taking 75 gm of H_2SO_4 and different weigh of Na_2SiO_3 at specific gravity of 1.10 and 1.2 respectively at room temperature (25 ^{0}C)

Table 4. 1: The Physical properties of the prepared silica gel samples obtained, by taking 75 gm of H2SO4 and different weigh of Na2SiO3 at specific gravity of 1.10 and 1.2 respectively at room temperature (25 ^{0}C)

Run No.	pH silicic acid sol	pH of Quenching water	Q_e (mg/g)	Wt. of Na_2SiO_3 (gm)	Wt. of silica gel obtained (gm)	Free moisture content (%)
1	3	4	48.84	100.1	14.2	2.4
2	3.5	4	47.825	105.8	14.4	2.2
3	3.99	4	46.7832	106.5	14.7	2.6
4	4.5	4	26.88	108.4	15.	3.4
5	3	9	47.62527	100.2	14	3.4
6	3.5	9	46.42534	105.9	14.3	4.9
7	4	9	25.2626	106.4	14.6	5.4
8	4.5	9	24.8539	108.3	15.2	4.3

The above table shows that there is no much significant change in yield of silica gel obtained by varying either the final pH of the silicic acid sol or the pH of quenching water. The yield of silica gel is directly proportional to the amount of Na_2SiO_3 used to reach the desired pH of silicic acid sol. Due to the amount of Na_2SiO_3 used is nearly the same for each samples because the silicic acid sol pH changes rapidliy after it reaches 2.5 so the yield cannot be affected by silicic acid sol pH between 3 to 4.5. The amount of MB dye adsorbed reaches maximum (48.84 mg/g) when the pH of the hydrosol and quenching water is 3 and 4 respectively. And the moisture content for this sample is also close to commercially available silica gels.

4.2 Experimental design analysis result

The studied experimental response is amount of dye adsorbed per grame of silica gel “Q_e” (mg/g), are given in Table 4.2

Table 4. 2: Effect of pH of silicic acid sol and caustic or acidic silica (Volume = 50 ml, Time = 60 min, Conc. of MB = 20 ppm , Temp. = 25 OC ,λ = 665 nm, pH = 10.06, wt. of adsorbent = 20 mg)

Run	PH of hydrosol	Type of Quenching water	Q_e (mg/g)
1	3	Acidic at pH 4	48.84
2	3.5	Acidic at pH 4	47.825
3	4	Acidic at pH 4	46.7832
4	4.5	Acidic at pH 4	26.88
5	3	Basic at pH 9	47.62527
6	3.5	Basic at pH 9	46.42534
7	4	Basic at pH 9	25.2626
8	4.5	Basic at pH 9	24.8539

Design expert 7.0.0 software was used to determine the optimal conditions of silica gel production from Ethiopia sand using sol-gel method to adsorb MB dye. General factorial method was used to investigate the effects of two independent factors. The first factor is pH of silicic acid sol coded with (A) with four levels (3, 3.5, 4 and 4.5) and the other one is pH of quenching water coded with (B) with two levels (4 and 9). The Amount of dye adsorbed Qe (mg/g) values measured for each samples were used to compute the model coefficients by using sequential model sum of squares.

statistical significance of the model and model variables will be determined at 5% probability level (α = 0.05). The result found after the data was put to Design-Expert in order of sequence, there has been found a single model that can be possibly fit or satisfy the factors significance. This possible choice of model was 2 Factorial model that fits the given data.

Table 4. 3: Sequential Model Sum of Squares

Source	**Sum of Squares**	**Df**	**Mean Square**	**F-value**	**p-Value Prob > F**	
Mean vs Total	24478.95	1	24478.95			
Linear vs Mean	1490.02	4	372.5	13.71	0.0003	
2FI vs Linear	298.10	3	99.37	1019.62	< 0.0001	Suggested
Residual	0.78	8	0.097			
Total	26267.84	16	1641.74			

The table above shows the study parameters of the two factors (pH of silicic acid sol (A) and pH of quenching water (B)), type of factor (Categorical), mean and standard deviation. What can be observed from the data above was, the model best choice becomes 2FI with a certain standard deviation error of each factor. The model standard deviation becomes 0.31.

From the ANOVA result of Table 4.4 the design expert each two factors individually, i.e. pH of silicic acid sol and pH of quenching water and the combination between them at the same time had a significant effect on the amount of MB dye adsorbed.

Table 4. 4 Analysis of variance table ANOVA

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-Value Prob > F**	
Model	1788.11	7	255.44	2621.21	< 0.0001	Significant
A-pH of silicic acid sol	1327.71	3	442.57	4541.36	< 0.0001	
B-pH of quenching water	162.31	1	162.31	1665.49	< 0.0001	
AB	298.10	3	99.37	1019.62	< 0.0001	
Pure Error	0.78	8				
Cor Total	1788.89	15				

4.2.1 Model equation Development

A model equation is a representative equation in which it represents the whole model with a single mathematical relation that helps to maximize response. The Amount of dye adsorbed Qe (mg/g) values measured for each samples were used by the software to compute the model and presented in equation (4.1). The equation shows that to adsorb the maximum amount of MB dye by silica gel the pH of silicic acid sol and pH of quenching water must be in the lower range.

Final Equation in Terms of Coded Factors:

$$Qe = 39.11 - 3.90 * A - 2.27 * A + 0.57 *A - 3.19 * B - 0.57 * AB +2.43 * AB +1.49 * AB \quad (4.1)$$

Where A - pH of silicic acid sol

B - pH of quinching water

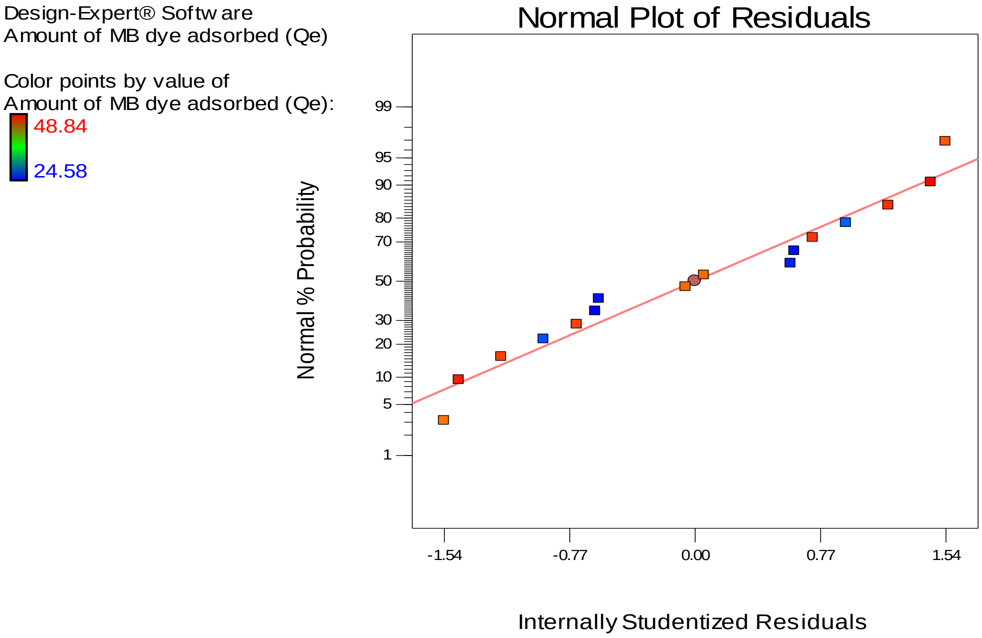
4.4.2. Model Adequacy Checking

From ANOVA results for response which is presented in the above figure confirms the adequacy of the 2FI model (the Model Prob > F is less than 0.05). Adeq-precision measures the signal to noise ratio and a ratio greater than 4 is desirable. The value obtained for production of silica gel for adsorption of MB dye was 107.841 this indicates an adequate signal. This model can be used to navigate the design.

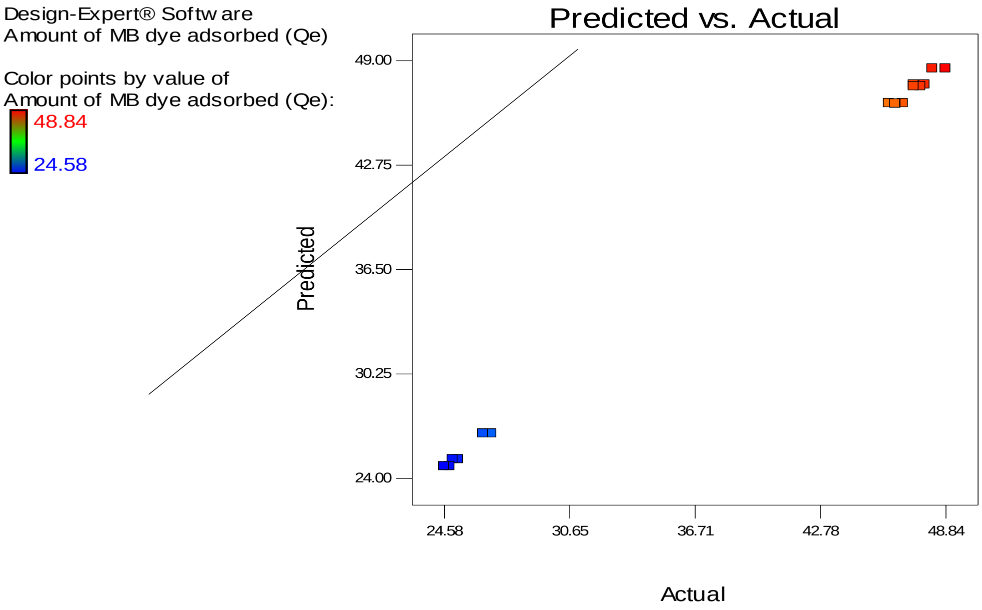
Table 4. 5: Model Adequacy value.

Std. Dev.	0.31	R-Squared	0.9996
Mean	39.11	Adj R-Squared	0.9992
C.V. %	0.80	Pred R-Squared	0.9983
PRESS	3.12	Adeq Precision	107.841

The value of correlation coefficient (R^2) of the model was 0.9996. This indicates that the regression were significant at a probability level of 99.96 %. In addition, the normal probability plots of the obtained residuals (Figure 4.1: a, b, and c) did not reveal anything particularly troublesome. A distribution plot of the residuals versus the predicted values of the response and a normal probability plot of residuals were created (Fig. 4.2.1 a, b, and c). The analysis shows the absence of any serious violation of the normality assumption. Subsequently, the analysis of variance was performed. Analysis of variance is an important statistical analysis and diagnostic tool which helps us to determine the statistical significance of regression.



(a)



(b)

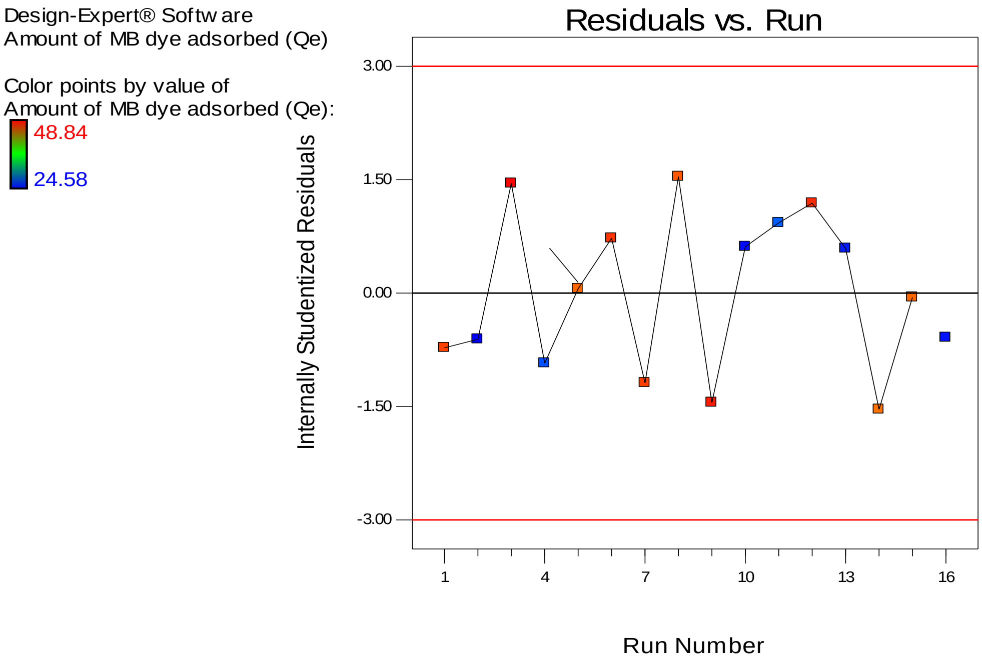


Figure 4.1: residual of accuracy of the response (Qe) (a) Normal plot of Rasedual, (b) Predicted vs. Actual, (c) Residual vs Run

4.3. Effect of individual factors on yield

The factors used in this analysis were pH of silicic acid sol and pH of quenching water.

4.3.1 Effect of pH of silicic acid sol on MB day adsorption capacity of silica gel

The effect of pH of silicic acid sol on MB dye removal efficiency of silica gel was presented in Figure 4.2. The pH at which the addition of sodium silicate solution was stopped and the resulting hydrosol was allowed to gel was found to have a profound effect on the characteristics of the prepared silica gel. The quality of silica gel was greatly affected by changes in the pH level of the hydrosol. The result in table 4.2 for both pH of quenching waters (4 and 9) shows that the highest adsorption capacity of MB dye 48.84 was recorded when final pH of the silicic acid sol is 3 and the minimum was recorded at pH of silicic acid sol is 4.5 is around 26.88. Since the adsorption capacity is directly proportional to the surface area of an adsorbent the silica gel prepared with this condition have a highest specific surface. This implies that the surface area increases when pH of silicic acid is at lowest pH, as a result higher available free sites are created when compared to the MB dye molocules so the highest removal efficiency will be obtained. The surface area increases in the acid solution, because at low pH the silica particles bear very little ionic charge and thus can collide and aggregate into chains and then gel networks. In the acid solution decreasing of OH will result in more siloxane linkages (Si - O- Si) change into silanol groups (Si - OH), so that colloidal suspension becomes more stable. Above pH 5, and up to 10.5, where silica begins to dissolve as silicate, the silica particles are negatively charged and repel each other. Therefore they do not collide, so that particle growth continues without aggregation. That is why higher porosity and lower surface area will be obtained in this situation.

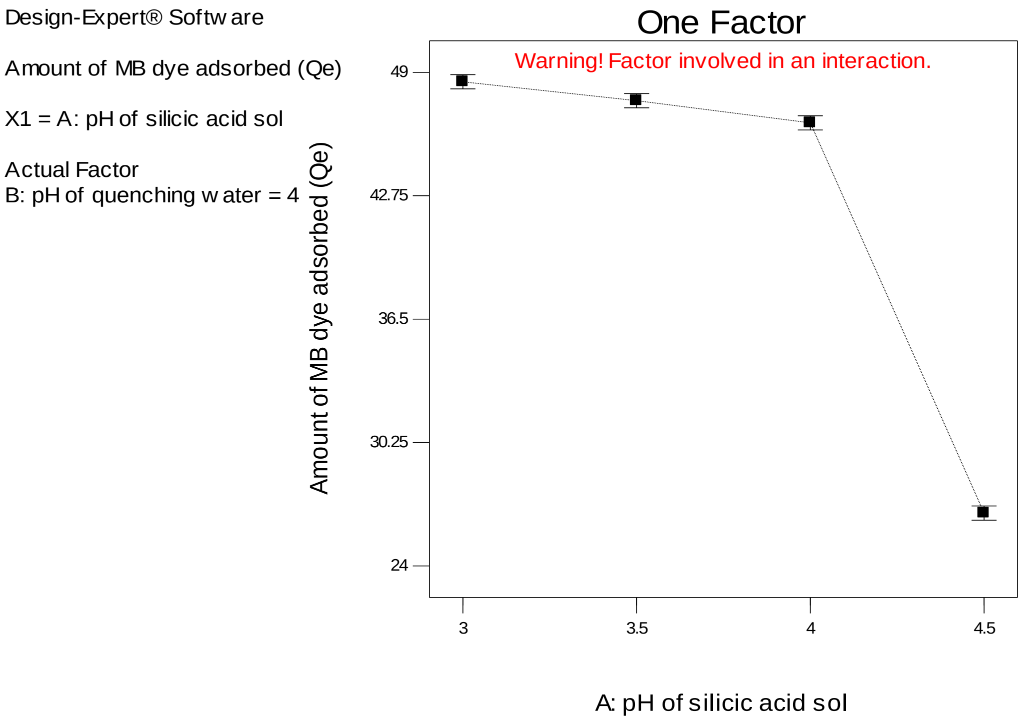


Figure 4.2: Effect of pH of silicic acid sol on adsorption amount of MB dye on silica gel

4.3.2 Effect of pH of quenching water on silica gel removal capacity of MB dye

The effect of pH of quenching water on silica gel adsorption capacity of MB dye was presented in Figure 4.4. For the case of adsorption of MB dye the performance of silica gel was not significantly affected. Rather it is affected by pH silicic acid sol.

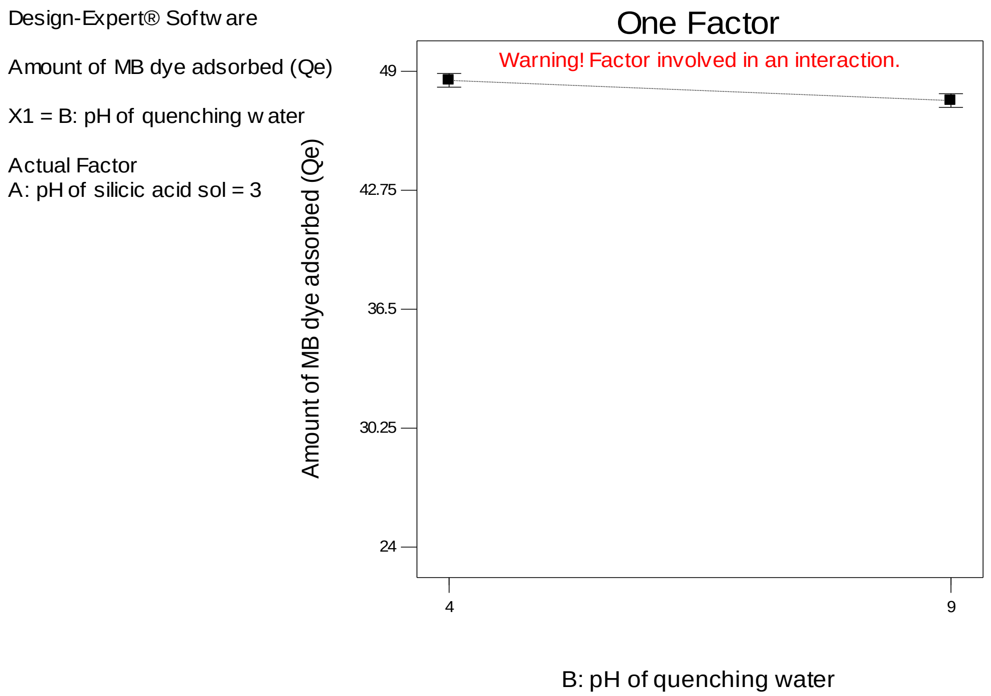
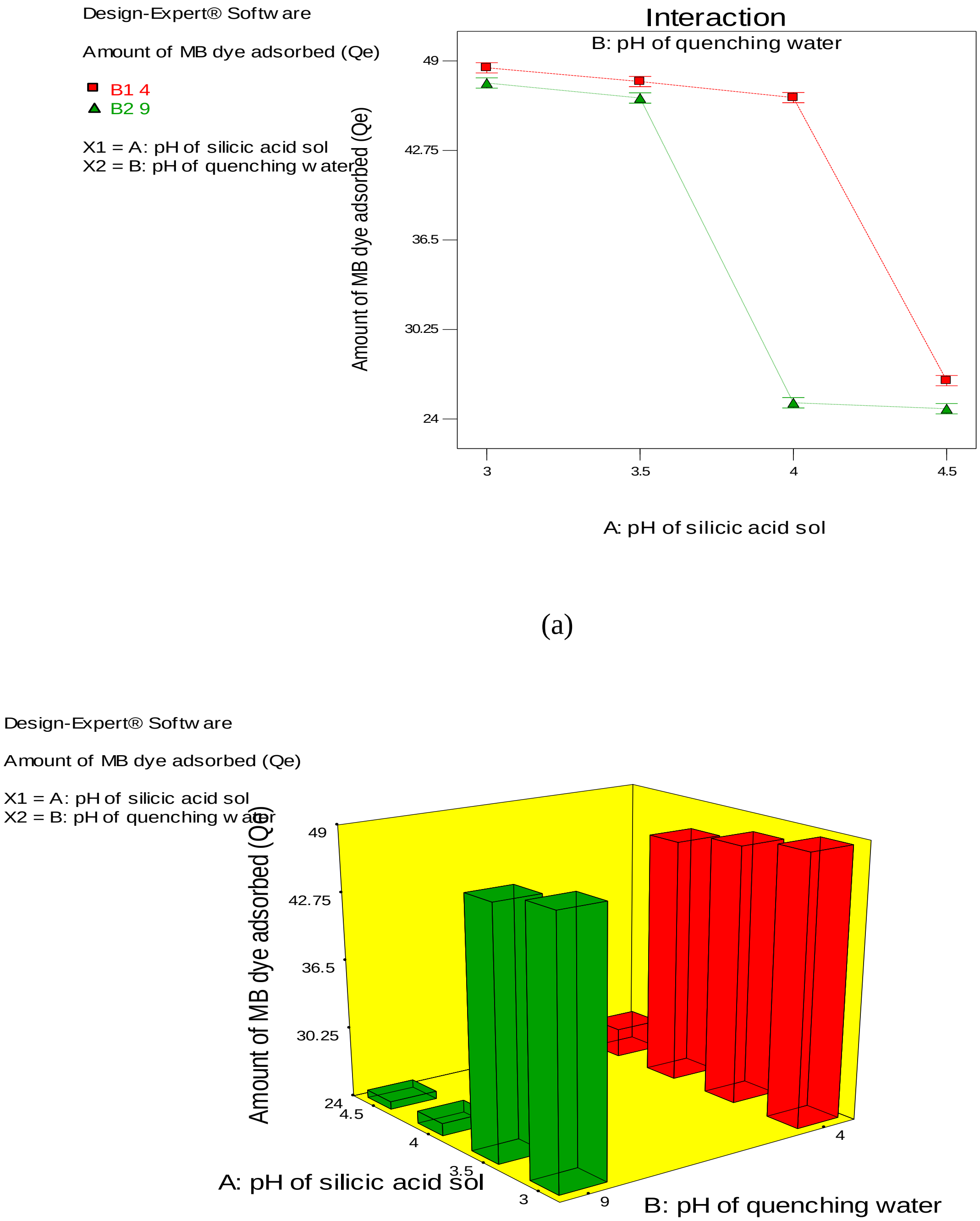


Figure 4.3: Effect of pH of quenching water on adsorption amount of MB dye on silica gel

4.3.3 Interaction effect on adsorption amount of MB dye on silica gel

The interaction (combined) effect of both factors were presented in Figure 4.4. The figure shows that the maximum adsorption capacity Qe was recorded 48.84 mg/g when the pH of silicic acid is at 3 and the pH of quenching water is at pH 4. And the minimum adsorption amount 24.85 mg/g recorded at pH of silicic acid is at 4.5 and the pH of quenching water is at pH 9.



(a)

(b)

Figure 4.4: Interaction (a), and (b), 3D curve

4.4 FTIR result of caustic and acidic silica gels

The chemical groups present in the synthesis caustic and acidic silica gel made from Ethiopian sand was checked by FT-IR analysis using Fig 4.6. For both of caustic as well as acidic gels as presented in the figure there are characteristic bands of silica gel at ~3400, ~1635, ~1098, 800, ~625 and ~468 cm^{-1}.The broad band at 3410cm-1to 3470 cm^{-1} is due to the stretching vibration of the O-H bond from the silanol groups (Si-OH) and physically adsorbed water (Javed et al 2011, Nayak 2010). The band at 1635 $cm^{-1}$is assigned to bending vibration of adsorbed water. The band at 1070 cm^{-1} to 1090cm-1 is due to the Si-O-Si asymmetric stretching vibration of oxygen atom in silicon atom while the band at 791cm^{-1} to 806 cm^{-1}has been assigned to the network Si-O-Si symmetric bond stretching vibration of oxygen atom in silicon atom (Nayak 2010).. The band at 461cm^{-1} to 476 cm^{-1} is associated with a network O-Si-O (SiO_4 tetrahedron) bond bending vibration modes (Javed et al 2011). The only difference between caustic and acidic silica gel is the presence of a band at 960 cm^{-1} in caustic silica gel but there is no evidence about the presence of this band in acidic gel. This happens because of using of caustic basified water in quenching step rather than acidified water. The band at ~960 cm^{-1} which is only present in the caustic gel is associated with stretching mode of Si-OH which is typical of gel structure (Almeida, R. and Pantano, G. (1990). The occurrence of absorption bands from the vibrations of the Si–O–Si bond, Si–O bond, Si-OH bond and O–H bond in the infrared spectrum indicates that the sample must be SiO_2. Therefore, the composition of the synthesized materials must be SiO_2 according to the above mentioned analysis of the infrared spectrum.

4.5 XRD analysis of caustic and acidic silica gels

XRD pattern of silica gel produced from sodium silicate was presented in figure 4.6. The major reflection or peaks of crystalline form of silica occur at Bragg 2θ angles of 20.856°, 26.636° and 36.541. It can be seen that no defined peaks corresponding to these Bragg 2θ angles are found in both the cases. A rather broad peak spanning 2θ angle at 21.4^0 and 23.4^0 was observed for caustic and acidic silica gels respectively which indicates that the material is amorphous and contains pure SiO_2 (Bhavornthanayod, C.and Rungrojchaiporn, P. (2009), J. Met. Mater. Miner. and Sooksaen, P., Suttiruengwong, S., Oniem, K., Ngamlamiad, K. and Atireklapwarodom, J. (2008).) The smoothness of the band also indicates that multiple washings with deionized water was efficient in removing the NaCl impurities trapped in the pores of the gel network. NaCl is formed during the hydrolysis, which must be eliminated because it destroys the gel network.

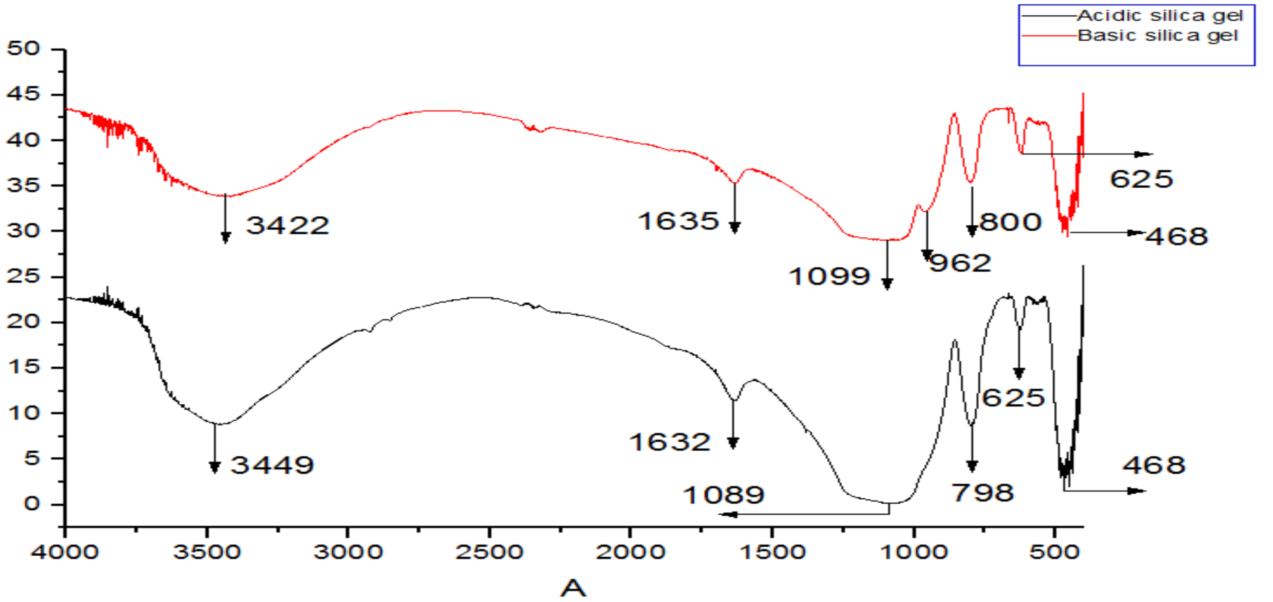


Figure 4.5: FTIR pattern of silica gel

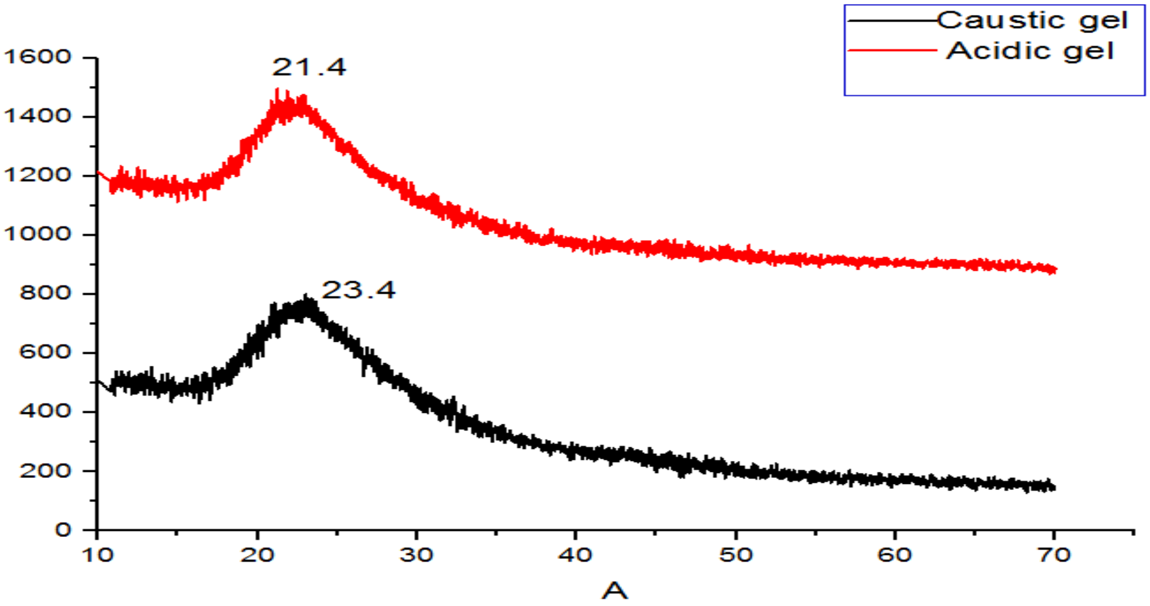


Figure 4. 6: XRD pattern of silica gel

4.6 Investigation of adsorption parameters

4.6.1 Effect of pH of silicic acid sol and pH of quenching water on MB dye adsorption

The effect of pH of silicic acid sol and pH of quenching water on adsorption capacity of MB dye was studied and the results are presented in Figure 4.7. the figure show that the highest removal efficiency was obtained by a silica gel prepared by using acidic quenching water (pH 4) and when the silicic acid sol is at pH = 3 and the adsorption capacity was 48.84 mg/g. So the rest adsorption parameters were studied by using this silica gel.

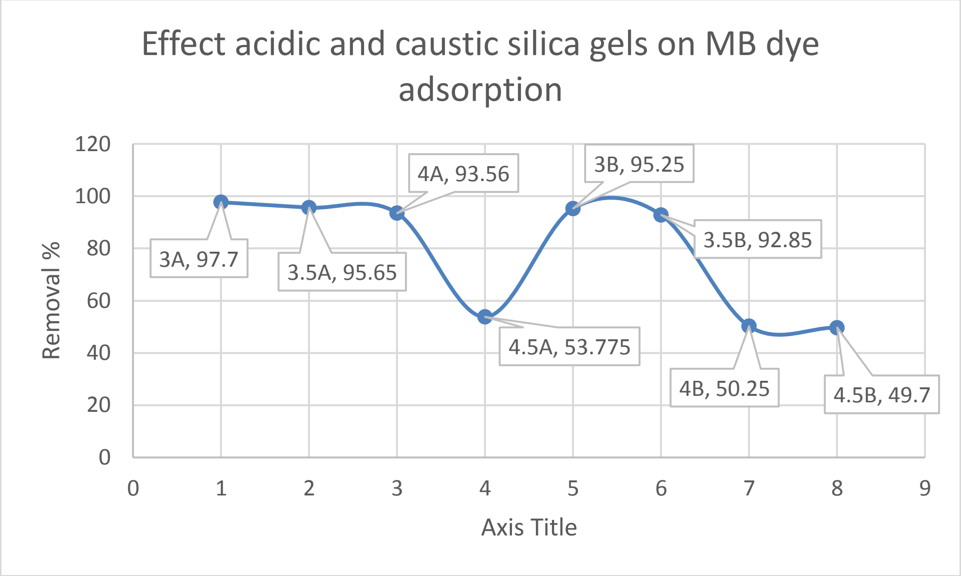


Figure 4. 7: Plot of adsorption capacity of silica gels produced in different conditions (Volume = 50 ml, Time = 60 min, Conc. of MB = 20 ppm , Temp. = 25 OC, λ = 665 nm, pH = 10.06, wt. of adsorbent = 20 mg

4.6.2 Effect of particle size on removal capacity of methylene blue dye

Adsorption of MB using silica gel on four sized particles ≥ 250, 250 ≤ 150, 150 ≤ 100 and ≤ 63 µm of adsorbents were studied. The results of variation of these particle sizes on dye adsorption are shown in Figure 4.8. It can be observed that the maximum removal capacity reaches 99.74% for particle size ≤ 63 µm and the minimum was for particle size ≥ 250 which is 77.94%. As the particle size increases the adsorption of dye decreases and hence the percentage removal of dye also decreases. This is due to the decrease in available surface area. For larger particles, the diffusion resistance to mass transfer is high and most of the internal surface of the particle may not be utilized for adsorption as a result the amount of dye adsorbed is small.

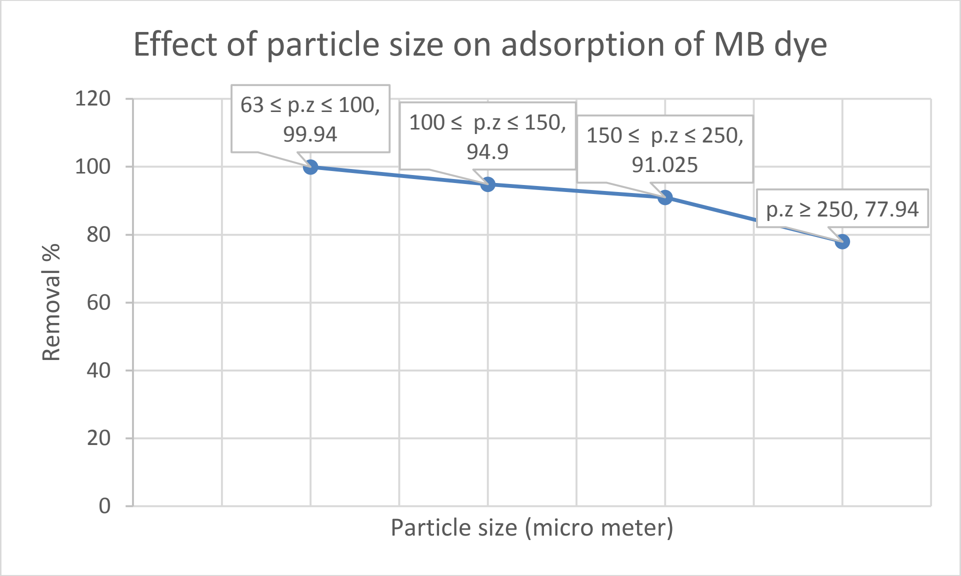


Figure 4. 8: Effect of particle size on MB adsorption (Volume = 50 ml, Time = 60 min., Wt. of adsorbent = 20, pH = 10.06, Temp. = 25 OC, Conc. MB = 20 ppm)

4.6.3 Effect of pH on Methylene blue day adsorption

The pH of a solution is an important factor that influences the adsorption capability of the adsorbent, particularly those having functional groups such as amino groups, which may be protonated or deprotonated easily to form various surface charges in solutions at varied pH. To observe the effect of pH on adsorption capability of prepared silica gel, the adsorption experiments were done in solutions with different pH values by doing other parameters constant. The result was presented in Figure 4.9. From the figure it can be observed that the removal of MB dye increases with increasing pH. The uptake attained its extreme at pH 10. At low pH the adsorption capacity of MB dye decreases, because of the presence of hydrogen ions which compete with cationic groups on MB for adsorption spots, thereby blocking the adsorption of dye. In addition under acidic condition the basic dye is protonated and the intensity of the positive charge is localized more on dye molecules leading to an electrostatic repulsion between adsorbent and adsorbate (Yang and Feng 2010)   as a result it causes a decrease in adsorption capacity.

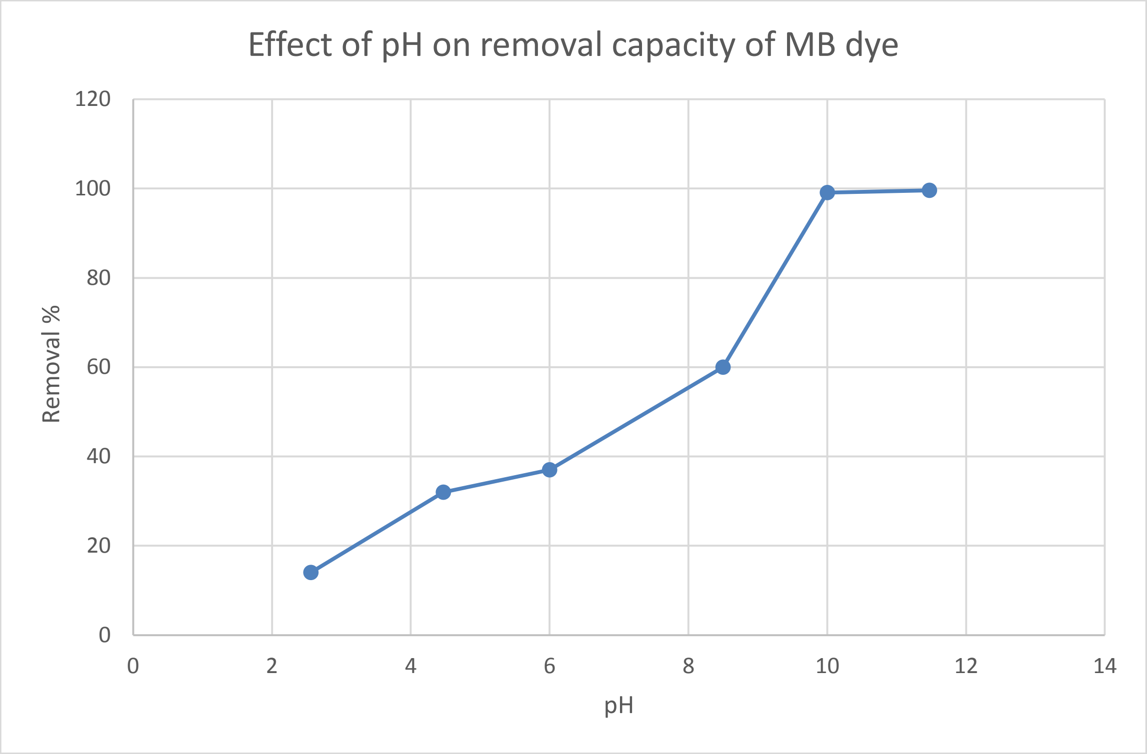


Figure 4. 9: Effect of pH on Methylene blue day adsorption. (Volume = 50 ml, Temp. = 30 OC, λ = 665 nm, Time = 30 min., Conc. MB = 15 ppm

4.6.4 Effect of temperature on Methylene blue dye adsorption

The effect of the temperature on MB adsorption capacity by silica gel was studied at 302.5 ^{O}K, 315.5 ^{O}K and 328 ^{O}K and the result was presented in Figure 4.10. The methylene blue concentration is fixed at Co = 20 ppm. The figure show that the adsorption capacity increases when the temperature decreases. The maximum adsorption (78.84) was achieved at 302.5 ^{O}K. This indicates that the adsorption of MB dye on silica gel follows exothermic process. This happens because increasing temperature may decrease the adsorptive forces between dyes and the active sites on the adsorbent surface as a result of decreasing adsorption capacity. (Chowdhury and Saha 2010; Salleh et al. 2011; Bharathi and Ramesh 2013).

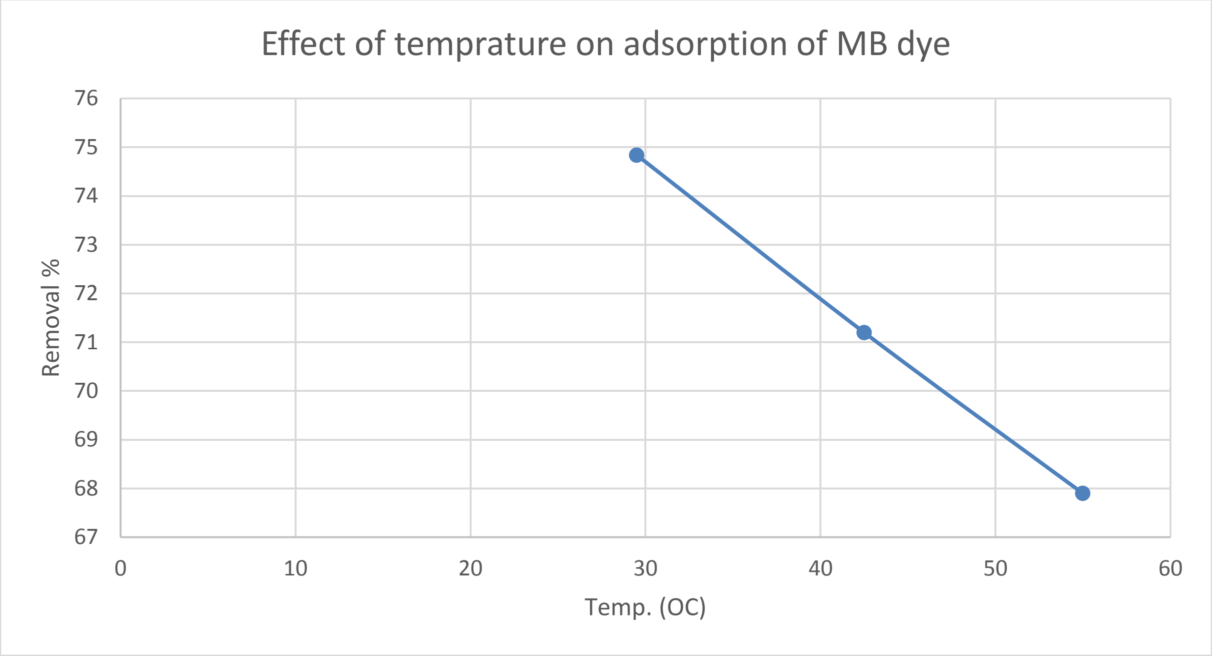


Figure 4. 10 Effect of temperature on Methylene blue dye adsorption. (Volume = 50 ml, Conc. of MB = 20 ppm , pH = 10.06, Time = 30 min., λ = 665 nm)

4.6.5 Effect of methylene blue day concentration

The effect of initial concentration of methylene blue day on the removal efficiency of silica gel was investigated over wide range of MB day concentration keeping other conditions as adsorbent dose, volume of solution, contact time, temperature and solution pH. The results are presented in figure 4.11 (a) and (b). From the figure we can say that the uptake of MB dye was rapid at lower concentration (5-10 mg/L) and as concentration increase the amount of MB dye adsorbed was decreased due to the fact that at lower concentration, the ratio of the initial number of MB day molecules to the available surface area is low and the available sites are high, but at high concentrations of dye, the available sites are fewer as a result the proportion removal of MB on silica gel was lowered from78.9 to 61.5. Amount of MB day adsorbed per unit mass of adsorbent increased from 9.23 to 35.756 mg/g with increasing MB day concentration increased from 5 to 25 mg/L. Since after a long period of time all the sites are occupied by the MB day molecules the adsorption become nearly constant whatsoever concentration of day is increased. This suggests forming a monolayer on the acidic silica gel.

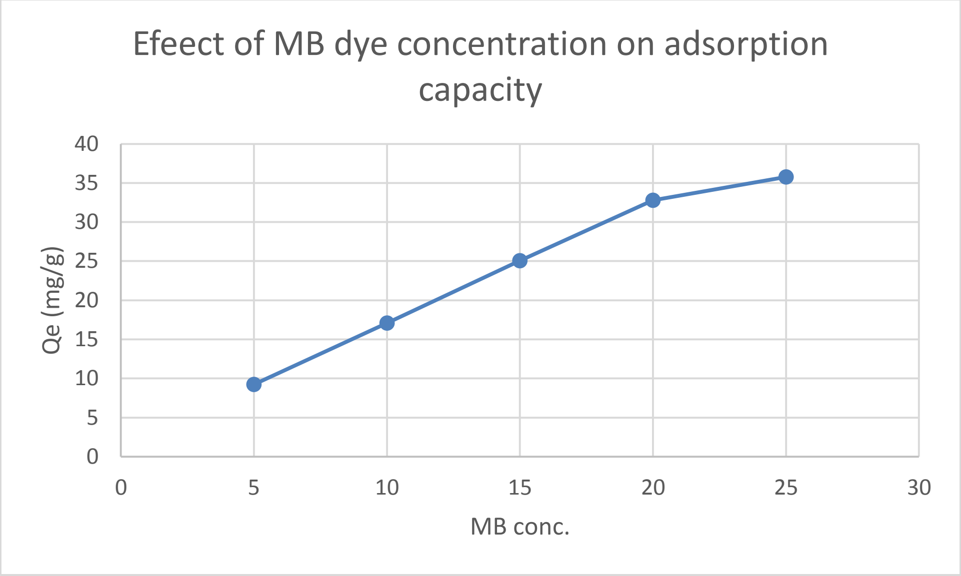


Figure 4. 11: Effect of methylene blue day concentration on adsorption capacity of MB dye silica gel. (Volume = 50 ml, Temp. = 25 OC, λ = 665 nm, time = 15 min., pH = 10.06

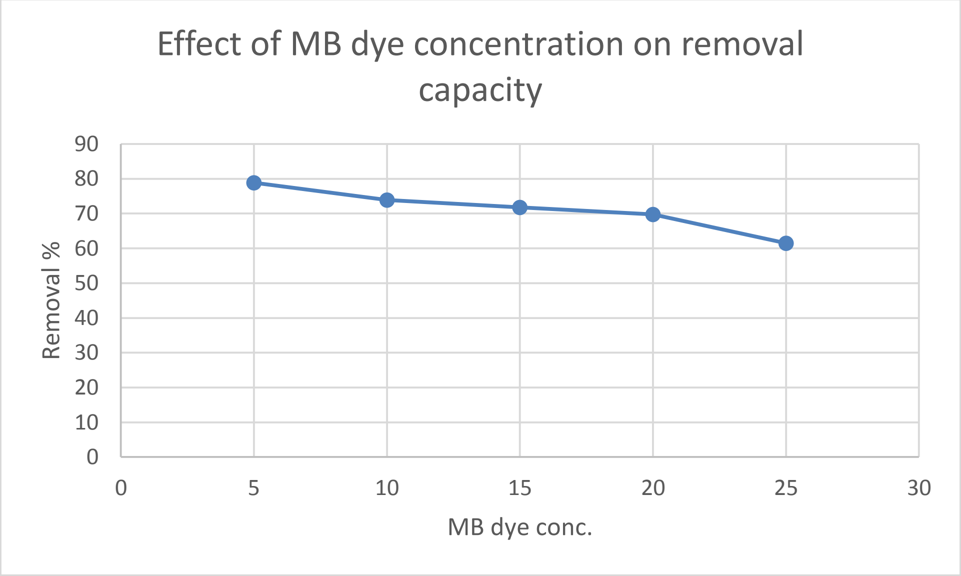


Figure 4. 12: Effect of methylene blue day concentration on Removal efficiency of MB dye by silica gel. (Volume = 50 ml, Temp. = 25 OC, λ = 665 nm, time = 15 min., pH = 10.06

4.6.6 Effect of dosage of adsorbent

The effect of the dosage of adsorbents on the removal efficiency of MB day on silica gel was studied. Initial concentration of methylene blue was preserved at 20 mg/L initial volume was 50 ml, pH was around 10.04, temperature is at 25 ^{O}C and the contact time of the adsorbent with the solution is 60 min. The result was presented in Figure 4.13. It can be noticed from the figure that the removal efficiency was greatly increased with increasing the dosage of the adsorbent until 0.021g beyond that the removal efficiency was not significantly affected with increasing dose of adsorbent. It shows that removal efficiency is 79.77% when the dose was 0.01 g, 92.3% for 0.015 g, 94.48% for 0.021g and 96.2 was for 0.05g. The increment in removal efficiency of MB day with increase of dose of silica gel is as a result of the increase in the number of adsorption sites relative to MB day molecules. As there was no drastic increase in the adsorption rate on increasing the dosage of adsorbent beyond 0.021g of silica gel, hence, from economic point of view, 0.021g was taken as optimum dosage for removal of methylene blue dye.

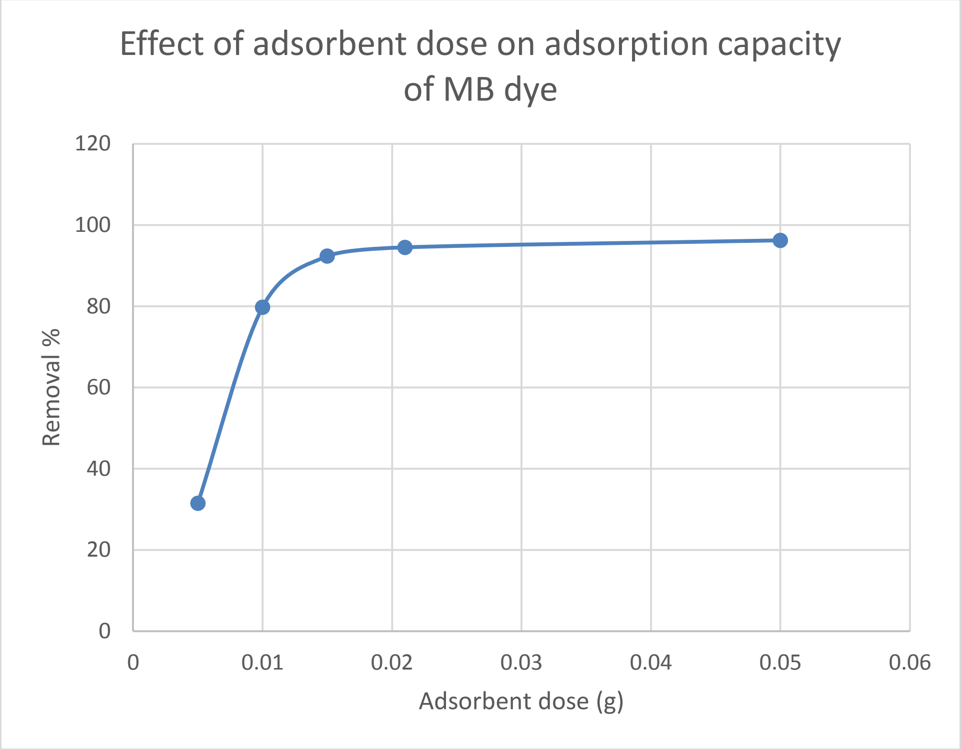


Figure 4. 13: Effect of methylene blue day concentration on adsorption. (Volume = 50 ml, Temp. = 25 OC, λ = 665 nm, time = 15 min., pH = 10.06

4.6.7 Effect of contact time on adsorption of Methylene blue dye

To know the time of maximum removal capacity of MB day on silica gel, the removal of MB day was studied as a function of time by using 0.02g adsorbent dose (silica gel) on 20 ppm initial concentration of MB day solution at pH around 10.06 in a fixed volume 50mL and adsorption temperature at 25^{o}C as shown in Figure 4.14. The MB day showed a rapid rate of adsorption for the first 20 minutes and the adsorption become insignificant after that, because of the most of the adsorption sites are occupied by MB day molecules and reaches at equilibrium after 210 min.. The adsorption capacity rate is high at the beginning due to large surface area of adsorbent available for adsorption of MB dye. At the beginning all reaction sites are vacant as a result the removal capacity is high. After the initial rapid adsorption, the adsorption rate was very slow almost reaching a constant value.

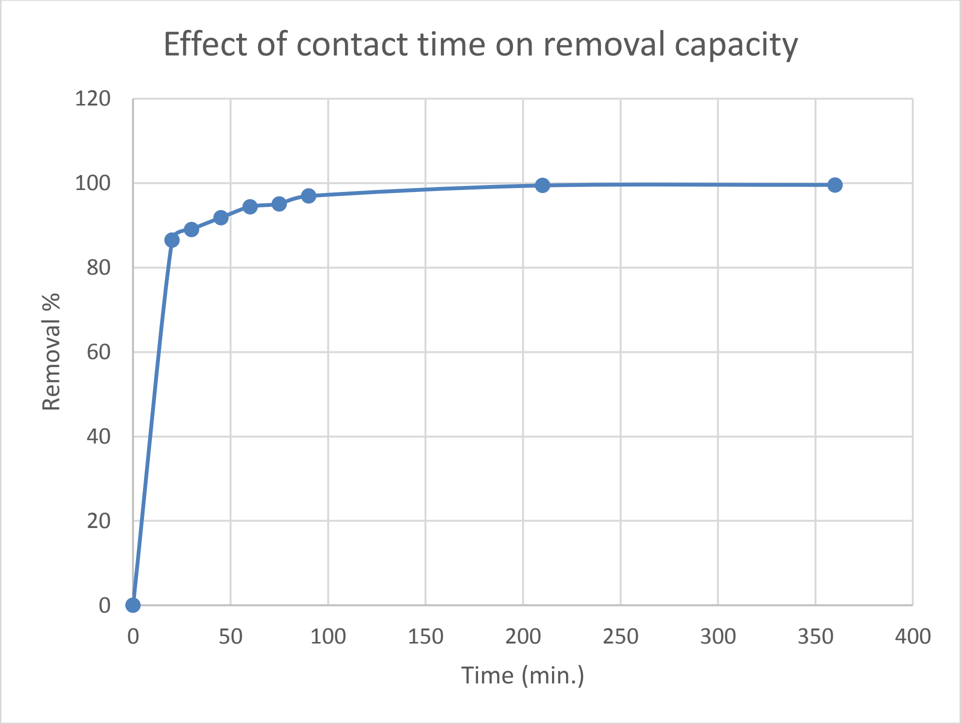


Figure 4. 14: Effect of contact time on contact time on adsorption. (Volume = 100 ml, Conc. of MB = 20 ppm Temp. = 30 OC, λ = 665 nm, pH = 10.06, wt. of adsorbent = 0.02g)

4.7 Adsorption isotherm of Methylene Blue dye

Adsorption study at equilibrium gives input about the capability of the adsorbent. An adsorption isotherm is described by specific values, which articulate the surface properties and affinity of the adsorbent and also be used to find the maximum adsorption capacity. Equilibrium data can be tested using commonly known adsorption methods. Several mathematical models can be used to describe the experimental data of adsorption isotherms. Models Langmuir, Freundlich and Temkin are used in the data analysis of the adsorption isotherm experiment.

4.7.1 Langmuir Adsorption Isotherm

According to equation (2.1), the values of Q_m and K_L were calculated from the slope and the y-intercept of the Langmuir plot of C_e / Q_e versus C_e. From the plot which is shown in Figure 4.15 amount adsorbed for monolyer formation (Q_m), Langmuir adsorption-desorption equilibrium constant (K_L) and regression constant (R^2) were detrmined and the values are presented in table 4.6.

Table 4.6: parameters and correlation coefficient of Langmuir isotherm model for adsorption of MB day on to silica gel

Langmuir isotherm model parameters				
Adsorbate	Parameters			
	Q_m (mg/g)	**K_L= (L/mg)**	**R_L**	**R^2**
Silica gel	58.45	0.176	0.185	0.9656

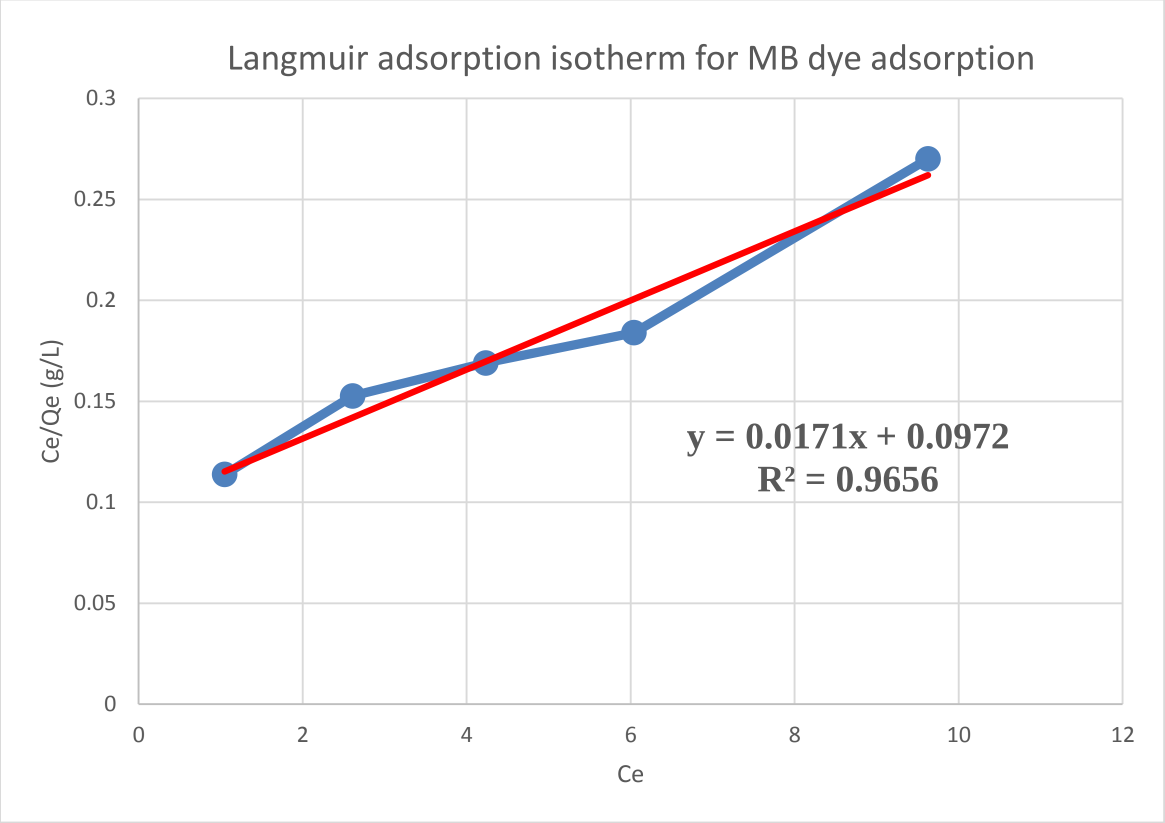


Figure 4.15: Langmuir plot for adsorption of MB dye on silica gel. (Volume = 50 ml, Temp. = 25 ^{O}C, λ = 665 nm, time = 15 min. pH = 10.06)

The R_L value in this investigation was calculated according to equation (2.2). It was found to be equal 0.185 at 25 ^{0}C which is between 0 and 1 indicating that the MB dye adsorption on silica gel is favourable.

4.7.2 Freundlich isotherm for MB sorption

The constants K_F and n were determined by using equation (2.3) by plot a graph of ln(Q_e) vs. ln

(C_e) as shown in Figure 4.16. Freundlich constants K_F and n and regression constant R^2 were determined by and values are shown in table

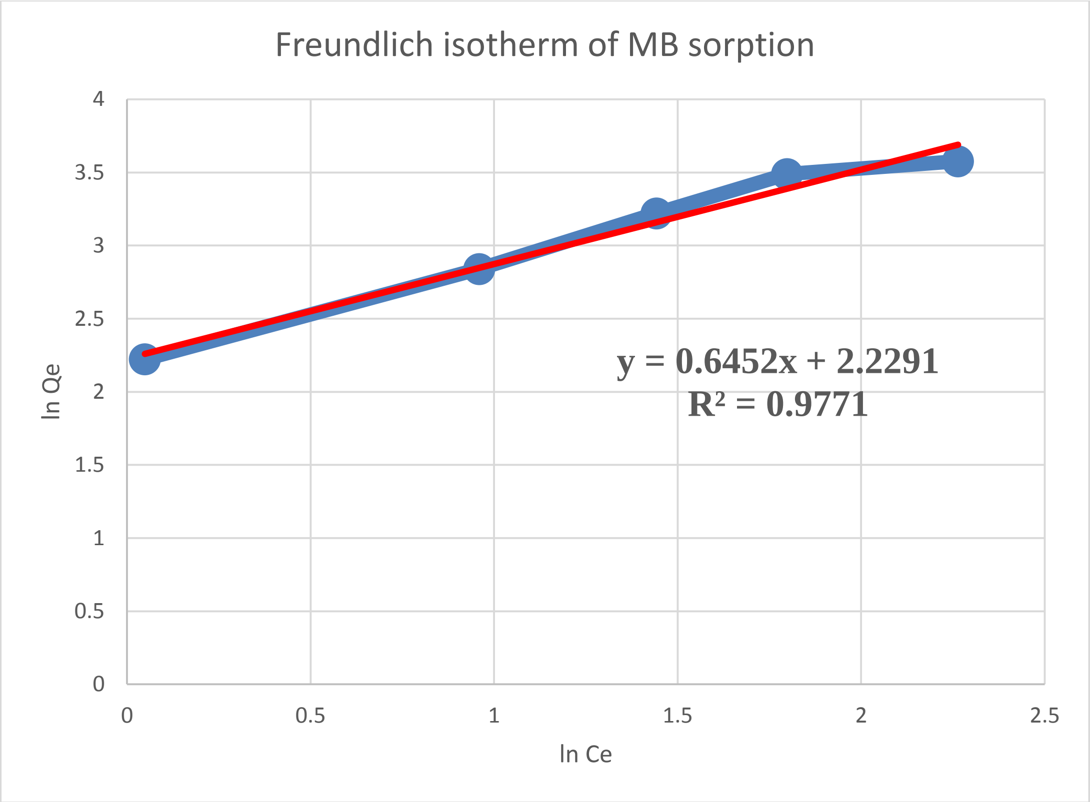


Figure 4.16: Freundlich plot for adsorption of MB dye on silica gel. (Volume = 50 ml, Temp. = 25 OC, λ = 665 nm, time = 15 min. pH = 10.06)

Table 4. 6: parameters and correlation coefficient of Freundlich isotherm model for adsorption of MB day on to silica gel

Freundlich isotherm model parameters				
Adsorbate	Parameters			
	1/n	**N**	**K_F= (mg/g)(L/mg)$^{1/n}$**	**R^2**
Silica gel	0.6452	1.55	9.29	0.9771

From the data in table 4.6, that value of 1/n = 0.6452 while n = 1.55 indicating that the sorption of MB day on silica gel is favourable and the R^2 value is 0.974.

4.7.3 Temkin Adsorption isotherm

According to equation a graph of Qe vs. ln Ce can be plotted as shown in Figure 4.17. The constants A, B and b were calculated using equation (2.5). All parameters and correlation coefficient are listed

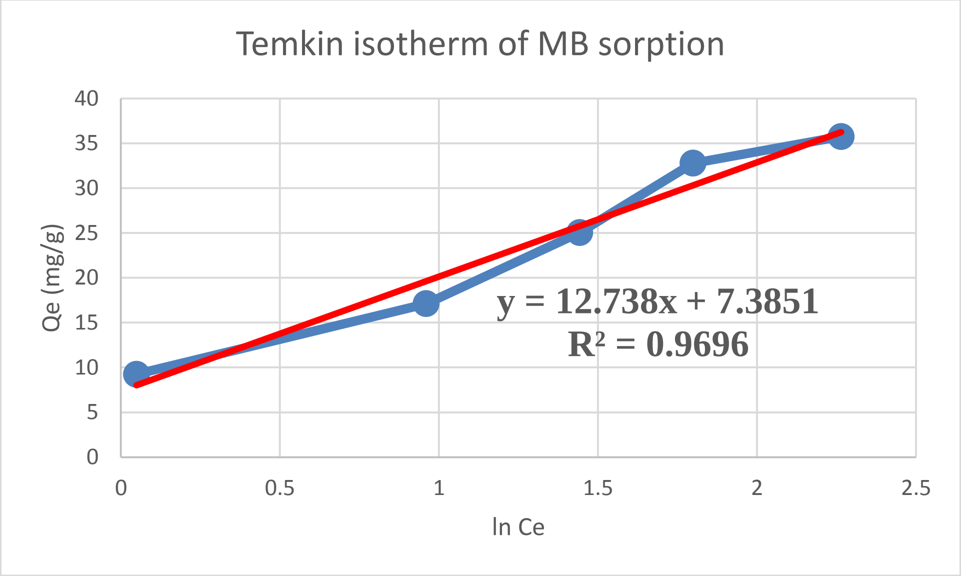


Figure 4. 17: Freundlich plot for adsorption of MB dye on silica gel. (Volume = 50 ml, Temp. = 25 OC, λ = 665 nm, time = 15 min. pH = 10.06)

Table 4. 7: parameters and correlation coefficient of Temkin isotherm model for adsorption of MB day on to silica gel

Temkin isotherm model parameters				
Adsorbate	Parameters			
	A_T (L/g)	**B (J/mol)**	**b_T**	**R^2**
Silica gel	1.786	194.5	12.738	0.9696

The three adsorption isotherm models Langmuir, Freundlich, and Temkin. were examined. From Langmuir isotherm data in Table 4.3.1 the value of R_L in this investigation was found to be 0.185 at 25 ^OC indicating that adsorption of MB dye on silica gel is favourable and R^2 value is 0.9656. From those three models Freundlich adsorption data has the greatest value of regression so that it is the most convinent from the others. From Freundlich isotherm data in Table 4.3.2 shows that the value of 1/n = 0.6452 while n = 1.55 so the adsorption of MB dye on silica gel is favourable and R^2 value is 0.9771. Larger value of n which means smaller value of 1/n indicates stronger interaction among adsorbent and adsorbate. 1/n between 0 and 1 is a measurement of the adsorption density heterogeneity of the surface, and it becomes more heterogeneous when 1/n becomes close to zero. From Temkin isotherm model R^2 is found to be 0.9696. This isotherm contains a factor that includes adsorbent-adsorbate interactions which indicate the presence of this interaction. The b values is lower than 80 KJ/mol which indicating a physical adsorption process.

4.8 Adsorption kinetics of methylene blue dye on silica gel

4.8.1 Pseudo-first-order adsorption kinetics

Rate constant for the adsorption of methylene blue from the dyeing effluent on adsorbent (silica gel) was specified depending on pseudo first-order equation (2.8). The pseudo first order rate constant was obtained by plotting a liner graph of linear graph of log ($Q_e - Q_t$) vs. time as shown in Figure 4.18. If the plot was linear with high correlation coefficient, this indicated that lagergren equation is proper to MB dye adsorption on silica gel, so the adsorption process is a pseudo first order. The Lagergren first order rate constant (K1) and Q_e specified from this model are presented in Table 4.8 with the corresponding correlation coefficient.

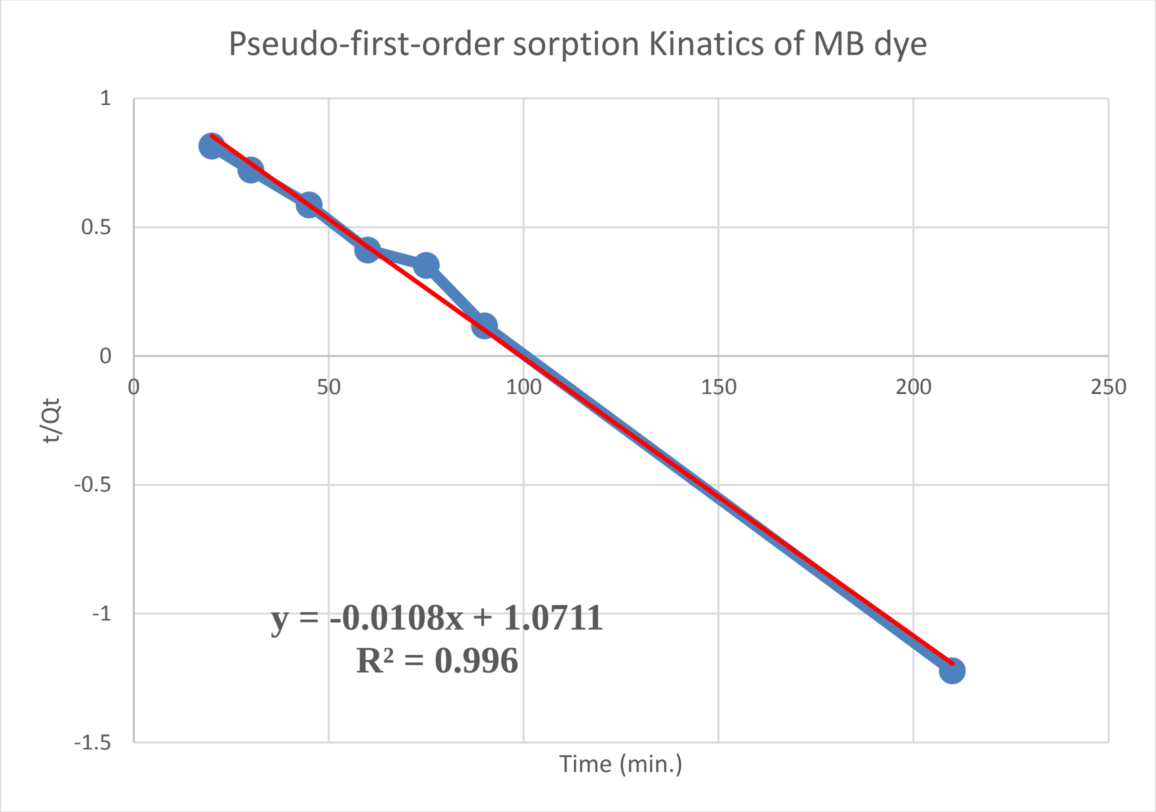


Figure 4. 18: Pseudo-first-order sorption kinetics on silica gel. (Volume = 100 ml, Conc. of MB = 20 ppm Temp. = 30 OC, λ = 665 nm, pH = 10.06, wt. of adsorbent = 0.02g)

The calculated Qe value does not match with the experimental Qe value Table 4.8. This pointed that the adsorption of MB dye does not obey the first-order kinetics therefore the pseudo first order model is not used to determine the first order rate constant (K_1) and (Q_e).

The results confirm that the pseudo second order kinetics model perfect fit the experimental date with linear regression coefficient which equals 0.999 (Figure 4.19).

4.8.2 Pseudo-second-order adsorption kinetics

The plot of t/Q_t versus time for the corresponding adsorbent is given in Figure 4.19. Q_e experimental and Q_e calculated values for pseudo second order kinetics model using equation (2.9) are illustrated in Table 4.8. it can be observed from that this table that there is an agreement between Q_e experimental and Q_e calculated values for the pseudo second order model.

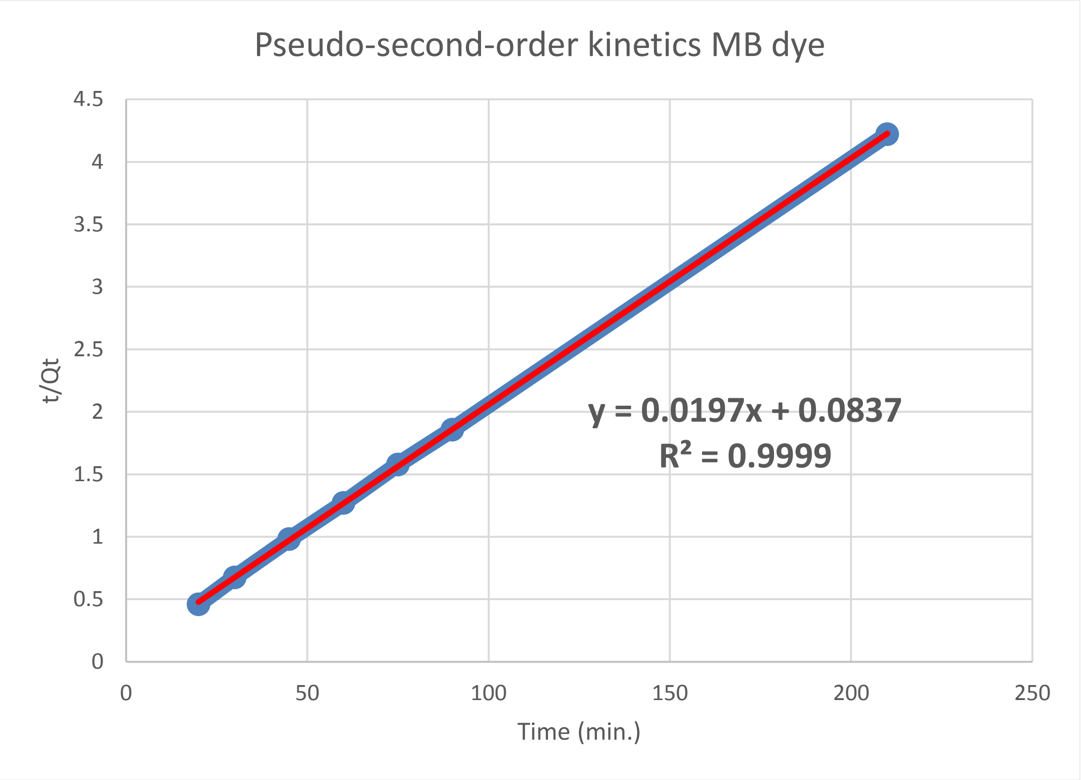


Figure 4. 19: Pseudo second order sorption kinetics of MB dye on silica gel. (Volume = 100 ml, Conc. of MB = 20 ppm Temp. = 30 OC, λ = 665 nm, pH = 10.06, wt. of adsorbent = 0.02g)

4.8.3 Intra-particle Diffusion

A plot of qt versus t 0.5 should be a linear line which pass through origin with a slope of K_{id} and intercept C when the adsorption mechanism follows the intra-particle diffusion model. The plot of qt versus $t^{0.5}$ for the corresponding adsorbent is given in Figure 4.20. The calculated values of Kid with the regression correlation coefficient are summarized in table 4.8. From the figure 4.20 it is clear that the graphs linear within certain range, but the trend of the data did not pass through the origin. The calculated values of K_{id} and C were 0.4233 mg/g.min and 42.027. The value of the intercept gives idea about the thickness of boundary layer i.e. the larger the intercept the larger the boundary layer effect. The deviation of the straight line from the origin may be due to the difference in the rate of mass transfer in the initial and final stage of the adsorption Process. Furthermore such deviation of the straight line from the origin indicates that pore diffusion is not the sole rate controlling step.

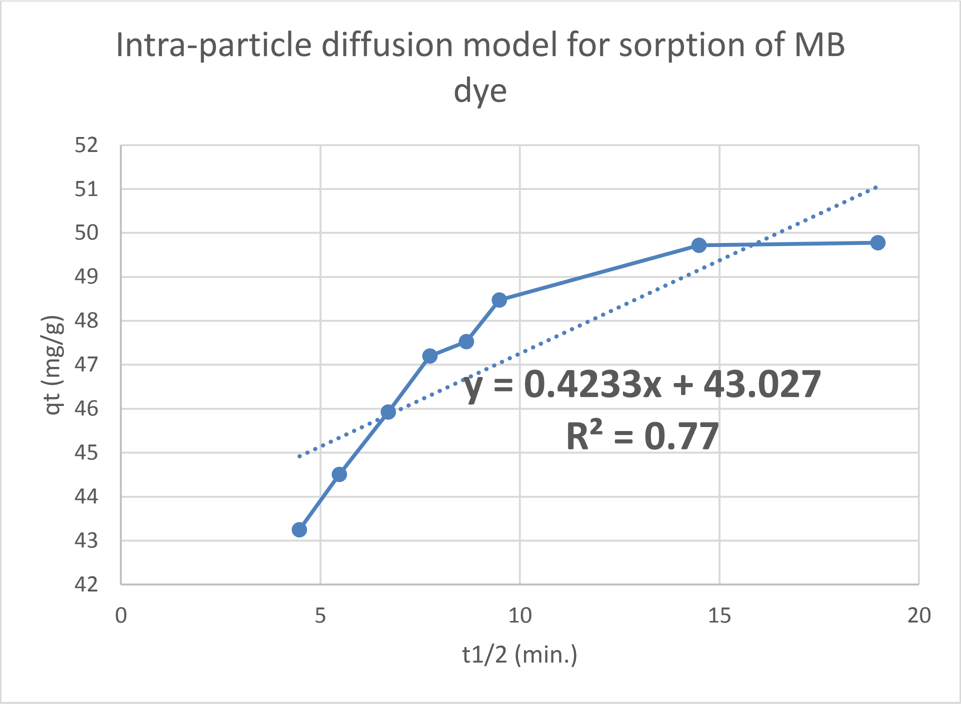


Figure 4. 20: intra-particle diffusion model of adsorption of MB dye on silica gel. (Volume = 100 ml, Conc. of MB = 20 ppm Temp. = 30 OC, λ = 665 nm, pH = 10.06, wt. of adsorbent = 0.02g)

Table 4. 8 Pseudo first order, Pseudo second order and intra-particle diffusion parameters for MB dye adsorption on to silica gel at 25 ^{O}C.

Adsorbent	$Q_{e\,(exp)}$ (mg/g)	Pseudo first order parameters			Pseudo second order parameters			intra-particle diffusion		
		K_1 (min^{-1})	**$Q_{e\,(calc)}$ (mg/g)**	**R^2**	**K_2 (g/mg min^{-1})**	**$Q_{e\,(calc)}$ (mg/g)**	**R^2**	K_{id}	C	**R^2**
Silica gel	49.78	0.025	11.78	0.996	4.63×10^{-3}	50.76	0.999	0.4223	42.027	0.77

4.9 Adsorption Thermodynamics

By using equation (4.2) and from the slope and y-intercepts Vant Hoff plot of ln Kd vs. 1/T Figure 4.21 ΔH and ΔS are determined. The distribution coefficient K_d was calculated from equation 4.2

$$K_d = \frac{V_s\,(C_o - C_e)}{m_{ads}C_e} \qquad (4.2)$$

Where Vs = volume of the solution (mL)

Co = initial concentration of adsorbate (mg/L)

Ce = the concentration of adsorbate at equilibrium (mg/L)

mads= mass of adsorbent dose (g)

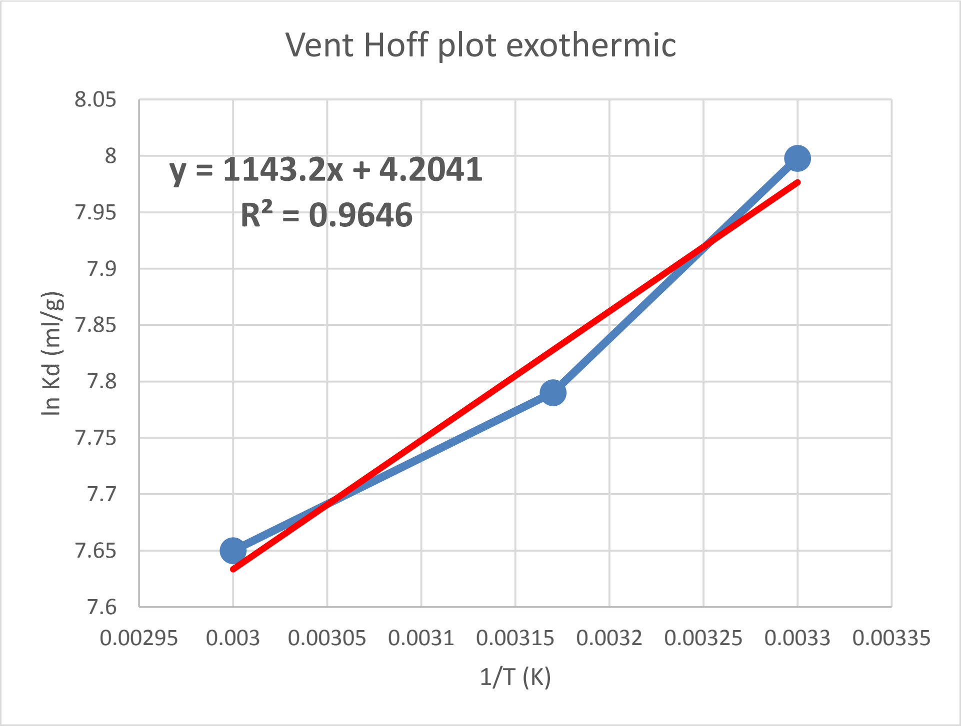


Figure 4.21: A graph of ln Kd vs. 1/T for MB dye adsorption on silica gel. (Volume = 50 ml, Conc. of MB = 20 ppm , pH = 10.06, Time = 30 min., λ = 665 nm)

The result presented that enthalpy of adsorption ΔH^o was 9.39 KJ/mol and ΔS^o was 94.61 J/mol.K. ΔG^o was calculated at different temperatures from the following equation:

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad 4.2$$

The calculated values are listed in table 4.9

Table 4.9: The values of the thermodynamic of MB dye adsorption at various temperatures

Adsorbent	**ΔH^o (KJ/mol)**	**ΔS^o (J/mol)**	**ΔG^o (J/mol)**		
			302.5 K.	315.5 K.	328 K.
Silica gel	9.5	34.95	-1067.82	-1522.16	-1959.0

The negative values of ΔG point that adsorption of methylene blue by silica gel is spontaneous and highly favourable adsorption. The negative values of ΔH reveal the exothermic nature of adsorption. The positive values of ΔS reveal increased disorder and randomness at the solid solution interface of the adsorbent (Demirbas 2009; Ping Ge 2011; Sharma and Das 2012).

5. CONCLUSTION

The preparation of a silica gel from Ethiopia sand with a high adsorption capacity of Methylene blue dye was the object of this work. Silica gels were obtained from sodium silicate solution mixed with sulfuric acid by sol-gel process. Preparation of silica gels depends on several factors. Two parameters are held: pH of silicic acid sol and pH of quenching water.

Amount of Methylene blue dye adsorbed Q_e (mg/g) represents the response of each gel prepared in all the studied experimental fields.

The analysis of variance of the response gave the coefficient R^2 to be higher than 95 % suggesting that the model is a good fit.

Factorial designs two variables with four levels and two levels respectively were chosen as the experimental designs. The results obtained after measuring the amount of Methylene blue dye adsorbed were fitted as 2 Factorial order equation and the corresponding interaction and 3D plots were plotted and analysed. The optimum silica gel having an important Methylene blue adsorption capacity (48.84 mg/g) was obtained by using pH silicic acid (pH = 3) and pH of quenching water (pH = 3).

After obtaining silica gel with high removal capacity the rest adsorption parameters are investigated using this acidic silica gel. Depending on the results, SiO_2 was able to remove rapidly within 15 min. with high removal efficiency at pH around 10, 0.02 g weight of dose and initial concentration of 20 mg/L MB dye solution. Around 94.5 % removal efficiency of MB dye was achieved. Around after 60 min at the same condition. Following conclusions can be made based on experimental data: it was found that adsorption of MB using silica gel was explained well by Freundlich model. Freundlich adsorption model has the highest regression (0.9771) and thus the best fit.

The Langmuir maximum Adsorption capacity Q_m and the RL value indicate that adsorption of MB dye on to silica gel is favour. Freundlich model parameters, values of 1/n and n showing that the adsorption of MB dye on silica gel is favourable.

The amount of MB dye adsorbed per gram of silica gel obtained by Lageregren pseudo second order model, Q_e (calc.) was in agreement with the experimental value, Q_e (exp.) indicates that chemisorption may be the rate limiting step where the valance forces are involved by electron sharing or exchange between the adsorbent and the adsorbate.

The negative ΔG^O values shows that the adsorption is favourable and spontaneous at these temperatures. The negative ΔH^O indicates that the adsorption is an exothermic process and points out that the adsorption is preferable at room temperature. ΔH value is lower than corresponds to chemical adsorption. This would suggest that this adsorption is a physical processes. Large ΔS^O positive value indicates that large structural changes takes place on the adsorbent and the entropy at the solid liquid interface in the adsorption system increases through adsorption processes.

Silica gel is a good effective adsorbent for the removal of MB dye from waste water. Since the two main raw materials for synthesise of silica gel sodium silicate and sulphuric acid are easily available in our country (Ethiopia) silica gel can be used as an effective adsorbent for treating industrial wastewater polluted with methylene blue under alkaline, low concentration of MB dye at temperature around 25 ^{O}C for removal over 85 %.

Recommendation:

This silica gel can be investigated in various application. Among these application as a catalyst support is one of its application that makes it attractive.

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Appendix

Data tables of Experiments

Volume = 50 ml

Time = 60 min.

pH = 10.06

Wt. of adsorbent = 20 mg

Data of Experiment 1: Effect of particle size

Temp. = 20 ^{O}C

Conc. MB = 20 ppm

Run	Particle size (μm)	Abs. after	C_f	% Removal
1	63 ≤ p.z ≤ 100	0.021	0.0117	99.94
2	100 ≤ p.z ≤ 150	0.142	1.02	94.9
3	150 ≤ p.z ≤ 250	0.235	1.8	91.025
4	p.z ≥ 250	0.549	4.41	77.94

Volume = 50 ml

Temp. = 30 ^{O}C

λ = 665 nm

Data of Experiment 2: Effect of pH

Time = 30 min.

Conc. MB = 15 ppm

Run	pH	Wt. adsorbent (g)	Abs. After	% Removal
1	2.56	0.05	1.75	14
2	4.47	0.051	1.3838	32
3	6	0.051	1.282	37
4	8.5	0.052	0.814	60
5	10	0.05	0.017	99.1
6	11.47	0.051	0.94	99.6
Average		0.02		

Volume = 50 ml

Conc. of MB = 20 ppm

pH = 10.06

Time = 30 min.

Data of Experiment 3: Effect of Temperature

λ = 665 nm

Temp. ^{O}C	Temp. K	Wt. of adsorbent (g)	Abs. After	% Removal	Ce (mg/L)	Kd (mL/g)	ln kd	1/T (1/K.)	ΔH (J/mol)	ΔS (J/mol.K)	ΔG (J/mol)
29.5	302.5	0.05	0.6234	74.84	5.032	2974.56	7.998	0.0033	9504.56	34.95	-1067.82
42.5	315.5	0.051	0.7108	71.2	5.76	2423.74	7.79	0.00317	9504.56	34.95	-1522.16
55	328	0.05	0.79	67.9	6.42	2115.26	7.65	0.003	9504.56	34.95	-1959.04

Volume = 50 ml

Conc. of MB = 20 ppm

Time = 60 min.

Temp. = 25 ^{O}C

Data of Experiment 4: Effect of Adsorbent Dose

λ = 665 nm

pH = 10.06

Run	Wt. dose (g)	Abs. After	% Removal
1	0.005	1.663	31.5
2	0.01	0.505	79.77
3	0.015	0.206	92.3
4	0.021	0.152	94.48
5	0.05	0.1108	96.2

Volume = 100 ml

Conc. of MB = 20 ppm

Temp. = 30 ^{O}C

Data of Experiment 5: Effect of Contact time

λ = 665 nm

pH = 10.06

wt. of adsorbent = 0.02g

Run	Time (min.)	Abs. After	% Removal
0	0	0	0
1	20	0.344	86.48
2	30	0.283	89.025
3	45	0.216	91.82
4	60	0.154	94.4
5	75	0.138	95.07
6	90	0.093	96.94
7	210	0.033	99.44
8	360	0.03	99.57

Volume = 50 ml

Temp. = 25 ^{O}C

Data of Experiment 6: Effect of MB dye concentration

λ = 665 nm

time = 15 min.

pH = 10.06

Run	Conc. MB (ppm)	wt. of adsorbent (g)	Abs. After	C_e	Q_e	% Removal
1	5	0.0214	0.1462	1.055	9.23	78.9
2	10	0.0216	0.333	2.611	17.1	73.89
3	15	0.0215	0.527	4.2315	25.043	71.79
4	20	0.0213	0.74456	6.04	32.77	69.79
5	25	0.0215	1.1746	9.625	35.756	61.5

Volume = 50 ml

Temp. = 25 ^{O}C

λ = 665 nm

time = 15 min.

Adsorption isotherm MB dye

pH = 10.06

Con. of MB (ppm)	Abs. After	C_e	% Removal	Q_e (mg/g)	C_e/Q_e	log Q_e	log C_e	ln C_e	ln Q_e
5	0.1462	1.055	78.9	9.23	0.11376	0.9652	0.02	0.0488	2.22
10	0.333	2.611	73.89	17.1	0.1527	1.233	0.417	0.9597	2.84
15	0.527	4.2315	71.79	25.043	0.169	1.4	0.626	1.442	3.22
20	0.74456	6.041	69.79	32.77	0.184	1.515	0.78	1.8	3.5
25	1.1746	9.625	61.5	35.756	0.27	1.55	0.983	2.264	3.577

Volume = 50 ml

Conc. of MB = 20 ppm

Temp. = 25 ^{O}C

Kinetics of MB dye

λ = 665 nm

pH = 10.06

wt. of adsorbent = 0.02g

Run	Time (min.)	Abs. After	C_t	Q_t	Q_e - Q_t	log (Q_e - Q_t)	t/Q_t	$t^{1/2}$
0	0	0	0	0	0	0	0	0
1	20	0.344	2.7	43.25	6.53	0.8149	0.46	4.472
2	30	0.283	2.195	44.51	5.27	0.7218	0.674	5.477
3	45	0.216	1.63	45.925	3.855	0.586	0.98	6.7
4	60	0.154	1.12	47.2	2.58	0.4116	1.27	7.746
5	75	0.138	0.987	47.53	2.25	0.352	1.578	8.66
6	90	0.093	0.612	48.47	1.31	0.117	1.857	9.487
7	210	0.033	0.112	49.72	0.06	-1.22185	4.22	14.49
8	360	0.03	0.087	49.78				18.97

Volume = 50 ml

Time = 60 min

Conc. of MB = 20 ppm

Temp. = 25 ^{O}C

Effect of pH of silicic acid sol and caustic or acidic silica gel

λ = 665 nm

pH = 10.06

wt. of adsorbent = 20 mg

Run	PH of hydrosol	Type of Quenching water	Q_e (mg/g)	% Removal
1	3	Acidic at pH 4	48.84	97.7
2	3.5	Acidic at pH 4	47.825	95.65
3	4	Acidic at pH 4	46.78	93.56
4	4.5	Acidic at pH 4	26.88	53.775
5	3	Basic at pH 9	47.625	95.25
6	3.5	Basic at pH 9	46.425	92.85
7	4	Basic at pH 9	25.26	50.25
8	4.5	Basic at pH 9	24.85	49.7