Removal of Methylene Blue from Aqueous Solution Using Ceramsite Synthesized from Dewatered Sewage Sludge, Bagasse Fly Ash and Bentonite

MELESE SIME

A Thesis Submitted to the Department of Applied Chemistry

School of Applied Natural Science

In partial fulfillment of the Requirements for the Degree of Master of Science in Applied Chemistry (Industrial Chemistry)

Office of Post Graduate Studies

Adama Science and Technology University

June, 2022

Adama, Ethiopia

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ADVISOR: ESHETU BEKELE (Ph.D.)

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DECLARATION

I hereby declare that this Master Thesis entitled **"Removal of Methylene Blue from Aqueous Solution Using Ceramsite Synthesized from Dewatered Sewage Sludge, Bagasse Fly Ash and Bentonite"** is my original work. That is, it has not been submitted for the award of any academic degree, diploma or certificate in any other university. All sources of materials that are used for this thesis have been duly acknowledged through citation.

MELESE SIME ________________________ ________________

Signature **Date**

RECOMMENDATION OF ADVISORS/ SUPERVISORS

I, the advisor of this thesis, hereby certify that I have read the revised version of the thesis entitled **"Removal of Methylene Blue from Aqueous Solution Using Ceramsite Synthesized from Dewatered Sewage Sludge, Bagasse Fly Ash and Bentonite"** by Melese Sime submitted in partial fulfillment of the requirements for the degree of Mater's of Science in applied chemistry (Industrial chemistry). Therefore, I recommend the submission of revised version of the thesis to the department following the applicable procedures.

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Major Advisor	**Signature**	**Date**

APPROVAL PAGE

I/we, the advisors of the thesis entitled **"Removal of Methylene Blue from Aqueous Solution Using Ceramsite Synthesized from Dewatered Sewage Sludge, Bagasse Fly Ash and Bentonite"** and developed by Melese Sime hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

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Major Advisor/Supervisor Signature Date

APPROVAL OF BOARD OF REVIEWERS

We, the undersigned, members of the Board of Examiners of the thesis by Melese Sime have read and evaluated the thesis entitled entitled **“Removal of Methylene Blue from Aqueous Solution Using Ceramsite Synthesized from Dewatered Sewage Sludge, Bagasse Fly Ash and Bentonite”** and examined the candidate during open defense. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the degree of Master of Science in Industrial chemistry.

Chairperson Signature Date

Internal Examiner Signature Date

Andualem Mekonnen (PhD) 

External Examiner Signature Date

Final approval and acceptance of the thesis is contingent upon submission of its final copy to the Office of Postgraduate Studies (OPGS) through the Department Graduate Council (DGC) and School Graduate Committee (SGC).

Department Head Signature Date

School Dean Signature Date

Office of Postgraduate Studies, Dean Signature Date

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LIST OF ACRONYMS AND ABBREVIATIONS

BFA	Bagasse Fly Ash
BOD	Biochemical Oxygen Demand
Ce	Equilibrium concentration of adsorbate (mg/L)
COD	Chemical Oxygen Demand
DSS	Dewatered sewage sludge
DO	Dissolved Oxygen
FTIR	Fourier transforms infrared
KL	Langmuir isotherm constant (L/mg)
MB	Methylene Blue
ppm	parts per million
qe	Amount of dye adsorbed per gram of the adsorbent at equilibrium (mg/g)
qm	Maximum monolayer coverage capacity (mg/g)
RL	Langmuir equilibrium parameter
SEM	Scanning electron microscopy
UN	United Nations
UV/vis	Ultraviolet Visible
V	Volume of the solution
WWF	World Wide Fund

ABSTRACT

Very recently, sewage sludge based ceramsite have been extensively used as low cost adsorbents in wastewater treatment. However, Sewage sludge based ceramsite usually has poor expansion performance and small specific surface area if only obtained from sewage sludge. This is beside of sewage sludge has low silica and alumina contents to ceramsite preparation. Therefore, in this study ceramsite prepared from sewage sludge and auxiliary materials, bagasse fly ash and bentonite was utilized as adsorbent to improve its adsorption efficiency towards removal of methylene blue dye from aqueous solution. The Ceramsite was prepared Under the optimal synthetic conditions (sewage sludge: bagasse ash: bentonite proportion was 40:30:40, preheating temperature of 250°C, preheating time of 20 min, sintering temperature of 600 °C, and sintering time of 30min). The prepared ceramsite were used for the removal of methylene blue from aqueous solution by adsorption mechanism. The physico-chemical and thermal characteristic of the prepared ceramsite before and after adsorption was characterized by UV/vis, *TGA, FT-IR, XRD and SEM analysis. During adsorption study effects of the contact time, adsorbent dose, pH, and initial dye concentration on the adsorption capacity of the ceramsite were studied. The kinetics and adsorption isotherm were also studied. The results showed that the adsorption capacity increased by increasing the pH of the solution, adsorbent dose and contact time, reached maximum at pH 8, adsorbent dose of 0.5g, contact time of 90min and initial dye concentration of 10(mg/L). Using optimum parameters; isotherm and kinetics of the adsorption process was analyzed using different model. The result showed that isotherm model of the process fitted well the Freundlich adsorption isotherm model and kinetics of adsorption is well defined by the pseudo-second-order. The maximum adsorption was found to be 9.884 (mg/g) and the efficiency of ceramsite prepared from sewage sludge, bagasse ash and bentonite to remove MB dye from aqueous solution at optimized condition was 99.8 %. The result clearly indicated the ceramsite prepared from sewage sludge, sugarcane fly ash and bentonite at optimized condition can be utilized to effectively remove MB dye from aqueous solution.*

Keywords: Methylene blue dye. Ceramsite, sewage sludge, sugarcane fly ash, bentonite, Adsorption isotherm; and Adsorption kinetics

1. INTRODUCTION

1.1. Background of Study

Many industries, such as dyestuffs, textile, paper, printing, cosmetics and plastics, use dyes in order to color their products and also consume substantial volumes of water. As a result, they generate a considerable amount of colored wastewater (Raja & Pasupathy, 2017). It is recognized that public perception of water quality is greatly influenced by the color. Color is the first contaminant to be recognized in wastewater (Y. Wang et al., 2020). The presence of very small amounts of dyes in water (less than 1 ppm) is highly visible and undesirable and may cause irregular coloration of surface waters as well as the pollution of the water with toxic compounds. Color stuff discharged from these industries poses certain hazards and environmental problems(Liu, Fan, & Li, 2018).

Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade (Yunusa & Ibrahim, 2019). Non-biodegradable nature of most of the dyes reduces aquatic diversity by blocking the passage of sunlight through the water and pose serious problems to the environment. This leads to reduced dissolved oxygen (DO) level in the water and may also increase the biochemical oxygen demand (BOD) of the contaminated water body (Mulana, Djuned, Fadli, & Meilian, 2020).

Methylene blue is one of cationic dyes, used in several industries such as textile, paper, leather, pulp, wool etc., for coloring their final products (Ozturk & Silah, 2020). Particularly, textile dyeing is becoming a major industry in Ethiopia consuming large quantity of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes (Samsami, Mohamadizaniani, Sarrafzadeh, Rene, & Firoozbahr, 2020). The effluents of these industries containing huge amount of dyes, discharged into water bodies cause severe damage to the environment. Acute exposure to methylene blue will cause increased heart rate, vomiting, shock, Heinz body formation, and tissue necrosis in humans (Abdulabbas, Bhaa, & Kamal, 2020). Thus, removal of MB dye from wastewater is of great concern from human and environmental point of view.

Some of the commonly used dye removal methods from wastewater are adsorption, coagulation, flocculation, ion-exchange, advanced oxidation, and membrane separation (Yuan, Cai, Liu, Huang, & Zhang, 2019). Among these techniques, adsorption is found to be an effective and economical method for dye removal from wastewater due to their versatility, easy operation, flexible design and growing availability of various types of eco-friendly and low- cost adsorbents. Low cost adsorbents such as bagasse fly ash, sewage sludge and banana peel were used as a form of activated carbon that has been processed to make it extremely porous and thus have a very large surface area available for adsorption or chemical reactions (Hafdi et al., 2020). Moreover, many other materials have been also investigated to determine their adsorption capacity for cationic methylene blue (MB) dye, such as, natural phosphate, zeolite, clay minerals (naturel, modified and extruded), lignite and activated carbon (Zhou, Zhou, Hu, Yan, & Yang, 2019). However, the major drawback of this kind of adsorbents is their high-cost, leaching of pollutants after adsorption, and difficulties of reusability. Therefore, the development of stable, cost effective, and reusable sorbent materials with greater efficiency for the removal of aquatic contaminants is still a priority area of scholars.

Adsorption of dyes using low cost adsorbents such as dewatered sewage sludge and bagasse fly ash has been used as a low-cost adsorbent to clean the wastewater prior to release to the environment (Kanawade, Gaikwad, & Misal, 2010). Moreover, Ceramsite is a common building aggregate, with high strength, thermal insulation, and acid-alkali resistance (J. Cheng et al., 2020; Kanawade et al., 2010; X. Zheng, Ji, Easa, Zhang, & Jiang, 2019). It is composed of multiple oxides, such as Fe_2O_3, Al_2O_3, and SiO_2, which can be used to prepare construction materials, that is, bricks, fine aggregates in concrete and ceramic materials, or as filter media in reactors for the treatment of municipal and industrial wastewater (Qin, Cui, Cui, Hussain, & Yang, 2015).

Dewatered sewage sludge (DSS) a by-product of the wastewater treatment plants (WWTPs), is considered as a part of the urban or industrial waste (Kharade, Suryavanshi, Gujar, & Deshmukh, 2014). It’s an inevitable byproduct of sewage treatment, with high moisture content, organic compounds, heavy metals, macronutrients, and microorganisms (Patel, Shankar, Khare, & Mondal, 2021). Besides, the disposal of DSS costs a lot, and the public demand for the sustainable management of wastes is increasing. The current practical disposal methods of DSS still depend on incineration, landfill, and application on the land (Lokeshwari & Joshi, 2014). However, the above disposal routes have severe short comings. For example, landfill requires huge tracts of land, and they may cause groundwater contamination (Yadav, Mishra, Kumar, & Paul, 2014). Thus, dealing with the increasing amounts of DSS has become an important environmental topic. Generally DSS contains water, organics, heavy metals, pathogenic bacteria and viruses, as well as 20~30% inorganic substances, which are mainly oxides or compounds of Si, Al, Fe and Ca. DSS may be used as partial or complete alternative to non-renewable natural resources for the preparation of ceramsite (G. Cheng, Li, Su, Sheng, & Fu, 2018). This is because its chemical composition is similar to that of shale, clay and other non-renewable natural resources used in making ceramsite (S. Chen, Chen, Pei, & Hou, 2019).

DSS based ceramsite prepared at high sintering temperature can not only realize the purposes of reduce, recycle and reuse of the waste sewage sludge, but also achieve the balance between economic and environmental benefits for the comprehensive utilization of DSS. Unfortunately, ceramsite usually has the poor expansion performance and small specific surface area if only obtained from DSS. Moreover, compared with shale, clay, coal fly ash or river sediment, DSS has also low silica and alumina contents for ceramsite preparation (T. Li, Sun, & Li, 2018). Hence, adding auxiliary materials, such as bagasse fly ash and bentonite containing high Si and Al.

Bagasse fly ash is a waste material obtained from the particular collection devices attached to the flue gas line of the sugar cane bagasse-fired boilers is considered as environmental pollutant for most sugar manufacturing industries. It is found to contain primarily silica (>65%) and alumina (>10%) and an important raw material for various applications (Udayanga et al., 2018). The utilization of bagasse fly ash in construction, removal of organic compounds (Qian & Jiang, 2014; T. Wang et al., 2018), heavy metals (Qin et al., 2015), and dyes (Kanawade et al., 2010). Bentonite is clay consists of smectite minerals like montmorrolonite, quartz, illite, kaolinite etc. It has exchangeable Na, Ca, or Mg cations, and exhibits far greater ion-exchange worldwide capacity than any other mineral except for zeolite. Bentonite has a good adsorption capacity for pollutants, and has been applied in the treatment of wastewater. Its high content of SiO_2 and Al_2O_3 makes bentonite meet the requirement as additives in making sewage sludge-based ceramsite. Therefore, Bagasse fly ash and bentonite are used as additives in making sewage sludge-based ceramsite.

The preparation of ceramsite from sewage sludge is beneficial to reduce the quantity of heavy metals leached from raw materials (Hu et al., 2021; Latosińska, Kowalik, & Gawdzik, 2021). Sewage sludge-based ceramsite can achieve the stabilization of heavy metals and reduce the pollution of heavy metals in the environment (Qi, Zhang, & Chen, 2015; Vickers, 2017). Therefore, in this study, Dewatered sewage sludge, Bagasse fly ash, and Bentonite were used in the preparation of ceramsite for removal of most widely used dye (Methylene blue) from wastewater.

1.2. Statement of problem

Wastewater containing dyes is undesirable since tiny amount of dye material destroy the aesthetic values of water. It is necessary to effectively treat effluent containing dyes due to the environmental and toxicology threats posed to human and aquatics.

There are different methods for the removal of dyes from wastewater effluents. The conventional methods can be categorized as biological, chemical and physical methods (Yuan et al., 2019). The biological treatment methods include activated sludge, trickling filters, anaerobic process, oxidation ponding; which have an advantage of eco-friendly nature, minimum usage of chemicals and energy saving but these methods is not effective for treating dyestuff wastewater because many commercial dyestuffs are toxic to micro-organisms being used in the treatment process. Biological treatment methods also require large land area and minimum flexibility in design and operation (Karthik, Saravanan, Bharathi, Dharanya, & Meiaraj, 2014b). Coagulation-flocculation, chemical precipitation, ion-exchange, ozone oxidation belongs to the group of chemical treatment methods, and dyes can be removed completely by this method. But these methods have the limitations of high energy demand, large consumption of chemical reagents, high cost, and require additional treatment before disposal (Monika, 2012). Physical treatment of wastewater includes membrane separation and adsorption techniques. Membrane separation has high separation efficiency, low energy consumption and easy operation as an advantage but have a downside of requiring special equipment, membrane fouling, and high investment cost (Yaseen & Scholz, 2019). The process of adsorption has an edge over the other methods due to its low regeneration cost, sludge free operation, simplicity of design and operation, less land area requirement, not affected by toxic chemicals and does not form harmful substances. Different adsorbent has been used to remove methylene blue from wastewater. But those adsorbents which have high removal capacity, low cost and easy accessibility are no question in being a choice for industrial wastewater treatment process. This research is intended to use low-cost adsorbent called sewage sludge. Sewage sludge which is a byproduct of wastewater treatment plants and bagasse fly ash, a waste collected from the particulate collection equipment attached to the bagasse fired boilers, cause a disposal problem. The management of this sludge and Bagasse fly ash has become important environmental issue due to stringent of environmental regulation and increasing public awareness. Reuse of the sludge as adsorbents; building, construction, ceramsite and cementitious materials; and land improvement additives such as structural soil improver have been reported (Babatunde & Zhao, 2007). DSS based ceramsite prepared at high sintering temperature can not only realize the purposes of reduce, recycle and reuse of the waste sewage sludge, but also achieve the balance between economic and environmental benefits for the comprehensive utilization of DSS. Unfortunately, ceramsite usually has the poor expansion performance and small specific surface area if only obtained from DSS. Moreover, compared with shale, clay, coal fly ash or river sediment, DSS has also low silica and alumina contents for ceramsite preparation (T. Li et al., 2018). Hence, adding auxiliary materials, such as bagasse fly ash and bentonite containing high Si and Al.

Bagasse fly ash is found to contain primarily silica (>65%) and alumina (>10%) and an important raw material for various applications (Udayanga et al., 2018). The utilization of bagasse fly ash in construction, removal of organic compounds (Qian & Jiang, 2014; T. Wang et al., 2018), heavy metals (Qin et al., 2015), and dyes (Kanawade et al., 2010). And bentonite is clay consists of smectite minerals like montmorrolonite, quartz, illite, kaolinite etc. It has exchangeable Na, Ca, or Mg cations, and exhibits far greater ion-exchange worldwide capacity than any other mineral except for zeolite. Bentonite has a good adsorption capacity for pollutants, and has been applied in the treatment of wastewater. Therefore, to best of my knowledge, the planned research were reuse, recycle and reduces waste material and to prepare ceramsite as adsorbent from sewage sludge and auxiliary materials, bagasse fly ash and bentonite was utilized as adsorbent to improve its adsorption efficiency towards removal of methylene blue dye from wastewater.

1.3. Objectives of the study

1.3.1. General objective

- ✓ Preparation and characterization of ceramsite from dewatered sewage sludge, bagasse fly ash and bentonite for use as an adsorbent for the removal of methylene blue from aqueous solution.

1.3.2. Specific objectives

- ✓ To prepare ceramsite from dewatered sewage sludge, bagasse fly ash and bentonite atoptimized condition of mixing ratio of materials, and sintering temperature.
- ✓ To characterize the ceramsite by using XRD, FTIR, SEM and TGA the ceramsite at the optimized conditions.
- ✓ To optimize pH, Contact time, adsorbent dose and initial conc. for efficient adsorption.
- ✓ To evaluate the MB removal efficiency of the ceramsite by varying pH, adsorbent dose,contact time and initial concentration for methylene blue removal from aqueous solution.
- ✓ Study the adsorption phenomena using kinetic and isotherm models.
- ✓ Evaluate its reusability potential of ceramsite at optimized condition.

1.4 Significance of the research

The major significance of this study includes but not limited to:-

- ➢ It can provide important baseline information's about the optimized condition for the preparation of ceramsite from dewatered sewage sludge, sugarcane bagasse fly ash and indigenous ceramic materials bentonite and their application in the removal of organic dyes from aqueous solutions. Ultimately, the result of this research work would be applicable for many of the industries for the treatment of wastewater.
- ➢ Generated fundamental knowledge on efficient waste management such as dewatered sewage sludge and sugar industry waste material that led to reduction of wasted resources that goes to nearby water bodies and landfills.

2. LITERATURE REVIEW

2.1. Ceramsite

Ceramsite is a common building aggregate, with high strength, thermal insulation, and acid-alkali resistance (Ji, Zheng, Chen, Lin, & Wu, 2015; X. Li et al., 2020; X. Zheng et al., 2019). Ceramsite is a kind of artificial mesoporous material with coarse and porous surface. Ceramsite is composed of multiple oxides, such as Fe_2O_3, Al_2O_3, and SiO_2, which can be used to prepare construction materials, that is, bricks, fine aggregates in concrete and ceramic materials, or as filter media in reactors for the treatment of municipal and industrial wastewater (Qin et al., 2015).(Yang, Lu, Jiang, & Zhang, 2014) used anthracite as foaming agent to prepare red mud-based ceramsite and studied the effect of anthracite on the red mud-based ceramsite properties. (Ma & Li, 2013)Prepared red mud-based ceramsite and studied the effect of sintering temperature on the properties of ceramsite. Besides, some researchers also prepared red mud-based ceramsite to remove pollutants in water, such as tetracycline and phosphate (Deng, Li, Yu, Wang, & Fan, 2019; L. Zhang et al., 2019). (Yang et al., 2014) Red Mud (RM)-based high-strength ceramsite was prepared using RM as the main raw material, coal fly ash and bentonite as auxiliary materials.

ceramsite has an elliptical shape with a particle size of 5.0~20.0 mm and can be prepared by a high-temperature sintering or sintering-free process (H. Wu et al., 2018; Y. Zhang et al., 2019). In recent years, due to its large specific surface area, low density, high porosity, light weight, developed microporous structure, hard texture and strong mechanical strength, ceramsite has been used as various plant bottom materials, toilet backfill material and filter material in garden flower, industrial architecture and wastewater treatment field, respectively (Cao, Wang, Sun, Jiang, & Zhang, 2016; X. Li, Shi, Yang, Xu, & Guo, 2019; Xie, Liu, Liu, Wang, & Huang, 2019). At present, the studies on ceramsite mainly focused on the optimization of preparation techniques and the selection of available raw materials. Ceramsite with lower density and higher water absorption and apparent porosity is favorable to be used as filter media. The high-temperature sintering process and chemical curing process (also known as sintering-free process) are currently the main preparation processes of ceramsite (Bao et al., 2016; L. Li et al., 2015). Generally, the high-temperature sintering process involves drying, smashing, sieving, mixing, pelleting, preheating, sintering and natural cooling (T. Li, Sun, Aftab, Fan, & Li, 2019; Zhu et al., 2020). The sintering conditions have a considerable impact on ceramsite properties in the preparation of ceramsite (Y. Chen et al., 2020), including four conditions-sintering temperature, sintering time, preheating temperature (H. Wu et al., 2018), and preheating time.

The sintering temperature is an important parameter that needs to be strictly controlled; a too low sintering temperature does not form enough liquid phases, whereas a too high sintering temperature forms excessive liquid phase, which can destroy the ceramsite structure, even causing the serious phenomenon of the adhesion. The properties of ceramsite also depend on preheating temperature. The main purposes of preheating the raw pellets are as follows(L. Zhang et al., 2019): (1) to remove moisture from the pellets to prevent their rupture during sintering; (2) after preheating, the amount of gas produced in the sintering stage can be controlled; and (3) to soften the surface of the pellets. In the high-temperature sintering process, ceramsite samples experience four different stages: In the first stage, when the temperature is over 100^{o}C, free water is evaporated; In the second stage, as the temperature further rises to 400~650^{o}C, water of crystallization and hydration is discharged and a lot of smoke and dust is released; in the third stage, when the temperature further rises to 900~1200^{o}C, a series of irreversible phase changes as well as physical and chemical changes take place;(Zhuang, Chen, & Ji, 2013) In the final stage of natural cooling, the enamel layer and pore structure are gradually formed.

In another study, the maximum sludge addition was 85%, but most of it was below 50% (Table 2.1). The heating rate was basically below 10°C·min^{-1}. The preheating temperature was 300–500 ◦C, and the preheating time was less than 30 min. The pyrolysis temperature was basically between 1000–1200 ◦C, and the pyrolysis time was 30 min or less (Table 2.1).

Table 2.1 Preparation methods and properties of ceramsite.

Sludge		Proportion of other materials (%)	Preheat		Pyrolysis		Reference
Type	Additive (%)		T (◦C)	Time (min)	T (◦C)	Time (min)	
WWTS	60	Fly ash (20), Gangue (20)	350	30	1200	30	(H. Wang, Xu, Liu, & Sheng, 2021)

WWTS	20	red mud (80	500	5–10	1000	20	(Wuyi & Huang, 2005)
WWTS	80	Bran powder (20)	300	20	950	30	(Wuyi & Huang, 2005)
WWTS	40	Marine mud (50), CaCO3 (10)	350	20	1120	10	(X. Wang et al., 2009)
WWTS	40	Bagasse ash (30) Bentonite (40)	250	20	600	30	This work

WWTS: wastewater treatment sludge

Traditionally, non-renewable natural resources, such as clay, shale, and other natural resources (Jiang, Jia, Zhang, He, & Kirumba, 2014), were employed for the preparation of ceramsite by the high-temperature sintering method (C. Wang, Wu, & Zhang, 2013).As shown in Table 2.2, the chemical composition of waste materials, including DSS, CFA, river sediment, and natural resources, such as shale and clay, was basically the same. Due to similar mineral contents, waste materials might be used as partial or complete alternative of natural resources for the preparation of ceramsite. This alternative method has exhibited several advantages such as (1) reducing or even abandoning non-renewable natural resources, up to the rigorous ecological and commercial demands for sustainability; and (2) providing an approach available for waste materials utilization, such as enhancing the utilization ratio of DSS.

Table 2.2 Composition of materials (%)

Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Ignition lose	References
DSS	7.5	2.3	6.9	2.9	0.5	0.1	0.5	72.4	(T. Li et al., 2018)
River sediment	52.5	17.6	5.1	1.5	1.8	0.5	2.8	8.5	(T. Li et al., 2018)
CFA	56.8	25.7	7.0	8.1	0.8	0.4	1.9	0.2	(T. Li et al.,

									2018)
Shale	32.2	3.15	1.36	23.6	0.45	0.38	0.47	35.2	(Azzam, Al-Ghazawi, & Al-Otoom, 2016)
Clay	47.1	35.06	0.32	0.28	2.79	ND	ND	14.45	(Kong et al., 2015)

ND: not detected

Dewatered sewage sludge (DSS) is a solid, semi-solid or liquid waste generated in the treatment process of municipal wastewater and industrial wastewater. Because of the accelerating urbanization process in China, DSS has been greatly increased due to increasing sewage discharge. It not only occupies large lands, but also causes the contamination of surface water and groundwater. Therefore, it is necessary to develop the comprehensive utilization of DSS.(Le, Julcour-Lebigue, & Delmas, 2015) Generally, DSS contains water, organics, heavy metals, pathogenic bacteria and viruses, as well as 20~30% inorganic substances, which are mainly oxides or compounds of Si, Al, Fe and Ca. DSS may be used as partial or complete alternative to non-renewable natural resources for the preparation of ceramsite,(S. Chen et al., 2019) because its chemical composition is similar to that of shale, clay and other non-renewable natural resources (Fu, Lin, & Chen, 2018).

DSS based ceramsite prepared at high sintering temperature can not only realize the purposes of reduce, recycle and reuse of the waste sewage sludge, but also achieve the balance between economic and environmental benefits for the comprehensive utilization of DSS. Unfortunately, ceramsite usually has the poor expansion performance and small specific surface area if only obtained from DSS. Moreover, compared with shale, clay, coal fly ash or river sediment, DSS has also low silica and alumina contents for ceramsite preparation (T. Li et al., 2018). Hence, adding auxiliary materials, such as bagasse fly ash and bentonite containing high Si and Al.

Bentonite

Bentonite is clay consists of smectite minerals like montmorrolonite, quartz, illite, kaolinite etc. It has exchangeable Na, Ca, or Mg cations, and exhibits far greater ion-exchange worldwide capacity than any other mineral except for zeolite. Na-bentonite has high swelling capacity and Ca- bentonite has a relatively low swelling capacity. Substitutions of silicon by cations produce an excess of negative charges in the lattice, which is balanced by cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) in the interlayer space. These cations are exchangeable due to their loose binding and, together with broken bonds (approximately 20% of exchange capacity) give montmorillonite (Adamis, Williams, & Fodor, 2005). The basic unit of montmorillonite crystals is an extended layer composed of an octahedral alumina sheet between two tetrahedral silica sheets. The stacks layers produce the montmorillonite crystals. Isomorphic substitutions in the octahedral sheet (few tetrahedral substitutions are observed in montmorillonite) create an excess of negative structural charge that is delocalized in the lattice. Cations located between two consecutive layers contribute to compensate the structural charge and to keep the layers bound. These cations can easily be exchanged, since they are retained by electrostatic attractions. The surface area associated with the basal surfaces of the extended unit is known as the interlayer surface when it corresponds to consecutive layers or as the external surface when it corresponds to the external basal surfaces of a crystal. The external and interlayer surface area represents approximately 95% of the total surface area of montmorillonite. On the other hand, the periodic structure of the montmorillonite crystals is interrupted at the edges, where the broken 13 bonds compensate their charge by the specific adsorption of protons and water molecules (WHO, 2005) Quartz is the most relevant accessory mineral in bentonite. Its structure is a tridimensional framework of silicate tetrahedral arranged sharing corners. In contrast with montmorillonite and kaolinite, quartz surface area is defined only as an external surface having broken bonds, which compensate charge by adsorption of protons or water molecules found in all the crystal phases. The kaolinite layers are formed only by a tetrahedral sheet of silica and an octahedral sheet of alumina, which contain almost no isomorphic substitutions. Hydroxyls of the octahedral sheet bind to oxygens of the tetrahedral sheet of the consecutive layer in the kaolinite crystal. The surface area of the kaolinite is thus reduced to external surface area and to edge surface area which similar to montmorillonite.

Table 2.3 chemical Composition of bentonite (%) (Mi, Yi, Wu, Xia, & Zhang, 2021).

Formula	Percentage
SiO_2	61.2

Al_2O_3	13.03
CaO	4.28
Fe_2O_3	7.72
K_2O	O.83
Na_2O	2.27
MgO	2.44

Bagasse fly ash

Bagasse fly ash is a waste collected from the particulate separation equipment attached to the flue gas line of the sugarcane bagasse-fired boilers. Sugar industry produces 30% bagasse for each lot of crushed sugar cane, the potential production capacity of burnt sugarcane bagasse residue is around 7–8% of total bagasse consumed (Madurwar, Mandavgane, & Ralegaonkar, 2014). The high percentage of silica and alumina in bagasse fly ash make it a good candidate for utilization as an inexpensive adsorbent for bulk use (Kharade et al., 2014). The bagasse fly ash is currently being used as filler in building materials (Kharade et al., 2014). It has been used previously for the COD removal from sugar mill and paper mill effluents (Lakdawala & Patel, 2012). Various researchers have utilized it for the adsorptive removal of phenolic compounds; metals and. studied the adsorptive removal of MG dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analyses. Batch adsorption studies were conducted to evaluate the effect of various parameters such as pH, adsorbent dose, contact time and initial MG concentration on the removal of MG. The initial pH of the dye solution strongly affected the chemistry of both the dye molecules and adsorbents in an aqueous solution. Equilibrium reached in about 4 h contact time. The adsorption followed pseudo-second-order Kinetics (Mall, Srivastava, Agarwal, & Mishra, 2005).

The removal of lead and copper from aqueous solution by bagasse fly ash was investigated under various experimental conditions, e.g. contact time, pH and temperature. The level of uptake of Pb^{2+} and Cu^{2+} by the fly ash generally increased, but not in a progressive manner, at higher pH values. The effect of temperature on the uptake of Pb^{2+} and Cu^{2+} revealed that the adsorption was enhanced on lowering the temperature. The experimental results emphasized the potential of fly ash for the recovery of metal ions from wastewater. The main mechanisms involved in the removal of heavy metal ions from solution were adsorption at the surface of the fly ash and precipitation (Gupta & Ali, 2004). Therefore, Bagasse fly ash and Bentonite will be used in the preparation of ceramsite for removal of most widely used dye (Methylene blue) from wastewater.

Table 2.4 chemical Composition of bagasse fly ash (%) (Kharade et al., 2014).

Formula	Percentage
SiO_2	72.75
Al_2O_3	10.63
CaO	6.835
Fe_2O_3	3.38
K_2O	3.805
Na_2O	2.095
MgO	1.575

2.2. Dyes

Dyes are ionic, aromatic organic compounds with structures including aryl rings with delocalized electron systems and also give color to the material. Mauveine, the first synthetic dye, was discovered in 1856 by William Henry Perkin (Khamparia & Jaspal, 2017). Since then, thousands of new synthetic dyes have been produced. Unlike most organic compounds, dyes possess color because they absorb light in the visible spectrum (400–700 nm), have at least one chromophore (color bearing group), have a conjugated system, i.e., a structure with alternating double and single bonds, and exhibit resonance of electrons, which is a stabilizing force in organic compounds. When any one of these features is lacking from the molecular structure the color is lost. In addition to chromophores, most dyes also contain groups known as auxochromes (color helpers), such as carboxylic acid, sulfonic acid, amino and hydroxyl groups. While these are not responsible for color, their presence can shift the color of a colorant and they are most often used to influence dye solubility. The largest consumer of these dyes is the textile industry accounting for around two thirds of its market. It is estimated that 1015% of the dye is lost during the dyeing process and released with the effluent (Yunusa & Ibrahim, 2019).

Dyes are usually classified based on their particle charge upon dissolution in aqueous application medium such as cationic (all basic dyes), anionic (direct, acid, and reactive dyes), and non-ionic (dispersed dyes) (Yagub, Sen, Afroze, & Ang, 2014). Anionic dyes are highly water soluble and difficult to remove by conventional methods. Nonionic dyes, also known as disperse dyes, do not ionize in an aqueous solution and their fused aromatic ring structure makes them highly resistant to degradation. However, a few cationic dyes like methyl blue can be easily removed by adsorption and advanced oxidation processes (Ahmad et al., 2015).

There are many harmful effects of dyes on ecosystem such as:

- ✓ They pose acute as well as chronic effects on most of the exposed organisms.
- ✓ They can absorb or reflect sunlight which enters the water bodies and thus affect the growth of bacteria and cause an imbalance in their biological activities.
- ✓ They have complex molecular structures which makes them difficult to treat with common municipal treatment operations.
- ✓ Consume dissolved oxygen and affect aquatic ecosystem

2.2.1. Methylene Blue dye

Methylene Blue (MB) is a heterocyclic aromatic chemical compound with molecular formula, $C_{16}H_{18}N_3SCl$, Fig 2.1,and chemical name [3, 7-bis (Dimethyl amino)-phenazathionium chloride Tetramethylthionine chloride]. MB is a basic aniline dye that forms a deep blue color in the oxidized state while it is colorless in its reduced form (leucomethylene blue). It is prepared by oxidizing dimethyl-phenylendiamine with ferric chloride in the presence of hydrogen sulphide (Sartape et al., 2017). It is utilized in coloring paper, dyeing cotton and wools, and coloring of paper stocks. It dissociates in aqueous solution in the same way that electrolytes dissociate into methylene blue cation and the chloride ion. The removal of methylene blue from any wastewater is most important due to the serious environmental damage that can occur as a result of contact with it, particularly in the case of human being (Mulana et al., 2020).

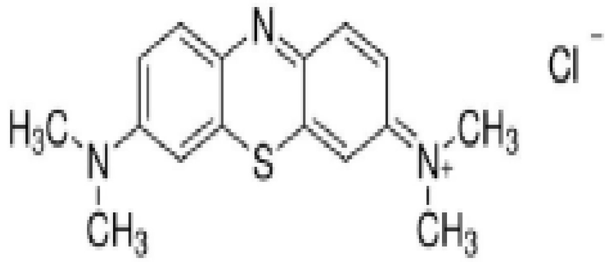
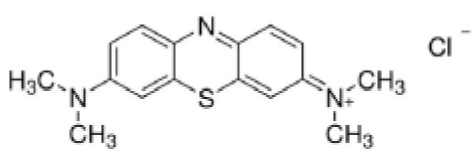


Figure 2.2 Molecular structure of Methylene blue (Sartape et al., 2017).

Properties of Methylene Blue

Table 2.3 Physical properties of Methylene blue

Molecular weight (M.W)	319.85222 g/mol
Molecular formula	$C_{16}H_{18}N_3SCl$
Solubility	Slightly soluble
Melting point	100-110°C (with decomposition)
Appearance	Dark green
Structure of MB 	3, 7-Bis (dimethylamino) phenothiazin-5-ium

2.3. Dye removal technologies

With the growing rate of industrialization, the emission of effluents from different industries poses serious threats to several living forms due to their adverse effects. The serious environmental impact and increase of public awareness in environmental protection, created a need to remove pollutants from wastewater before it is discharged into the environment. Currently there are several methods that can be used in the removal of dyes from industrial effluents. However, due to the variety of existent dyes and to the effluent's complexity, not all methods have the same efficiency and each method has its limitations. Generally, the treatment methods can be divided into three main categories namely physical, chemical and biological methods (Yuan et al., 2019).

2.3.1. Physical method

A number of different physical methods are used such as membrane-filtration processes (Reverse osmosis, electro dialysis, and Nano-filtration) and various adsorption techniques. The major disadvantage associated with the membrane filtration processes is that they have a limited lifetime, the problem of membrane fouling and the cost of periodic replacement must thus be included in any analysis of their economic viability (L. Zheng, Wang, & Wang, 2015). The process of adsorption has an edge over the other methods due to its sludge free clean operation, completely removed dyes, convenience operation and simplicity of design. Some physical methods are discussed below.

Membrane separation

Membrane separation process is the method that uses the membrane's micro pores to filter and makes use of membrane's selective permeability to separate certain substances in wastewater. Membrane separation has high separation efficiency, low energy consumption, easy operation, and no pollution and so on. However, this technology is still not large-scale promoted because it has the limitation of requiring special equipment, and having high investment and the problem of membrane fouling (L. Zheng et al., 2015). The important membrane separation processes are reverse osmosis and Nano-filtration.

Reverse Osmosis is a technology that is used to remove a large majority of contaminants from wastewater by pushing the wastewater under pressure through a semi-permeable membrane. Its permits the removal of all mineral salts, hydrolyzed reactive dyes, and chemical auxiliaries (L. Zheng et al., 2015).

Nano-filtration has been applied for the treatment of colored effluents from the textile industry. Nano-filtration membranes retain low molecular weight organic compounds, divalent ions, large monovalent ions, hydrolyzed reactive dyes, and dyeing auxiliaries. The treatment of dyeing wastewater by Nano-filtration is also used for the treatment of solutions with highly concentrated and complex solutions (Ghaly, Ananthashankar, Alhattab, & Ramakrishnan, 2014).

2.3.2. Chemical method

Chemical methods include coagulation-flocculation, precipitation, and coagulation, conventional oxidation methods by oxidizing agents such as ozone, irradiation or electrochemical processes

(Karthik, Saravanan, Bharathi, Dharanya, & Meiaraj, 2014a). Dyes can be removed completely by this process, it is expensive and also accumulation of concentrated sludge creates another disposal problem. Recently, new emerging techniques, known as advanced oxidation process, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for the pollutant degradation. But these methods are still costly & commercially unattractive. Common problems in these methods are the high electrical energy demand and the consumption of chemical reagents (Monika, 2012). Common chemical methods are discussed below.

Coagulation- flocculation

Coagulation -flocculation is one of the most used methods, especially in the conventional treatment process. Coagulation includes the use of suitable chemicals, through a chemical reaction, forms an insoluble end product. Active on suspended matter, colloidal type of very small size have electrical charge resulting in repulsion and prevent their aggregation. Adding in water coagulants such as aluminum sulphate, ferric sulphate, ferric chloride, giving hydrolysable metallic ions or organic hydrolysable polymers (polyelectrolyte) can eliminate the surface electrical charges of the colloids. This effect is called coagulation (Ayeche, 2012). Normally the colloids bring negative charges so the coagulants are usually inorganic or organic cationic coagulants. The metallic hydroxides and the organic polymers, besides giving the coagulation, can help the particle aggregation into flocks, thereby increasing the sedimentation (Ahmad et al., 2015).

The combined action of coagulation, flocculation and settling is named clariflocculation. Settling needs stillness and flow velocity, so these three processes need different reactions tanks. This processes use mechanical separation among heterogeneous matters, while the dissolved matter is not well removed (clariflocculation can eliminate a part of it by absorption into the flocks). The dissolved matter can be better removed by biological or by other physical chemical processes. But additional chemical load on the effluent (which normally increases salt concentration) increases the sludge production and leads to the uncompleted dye removal.

Chemical precipitation

Chemical precipitation is a relatively simple wastewater treatment technique in which chemicals such as sulphides, hydroxides and carbonates react with organic and inorganic pollutants present in wastewater to form insoluble precipitates. Chemicals react with dissolved dye molecules to form insoluble precipitates and then can be removed. The general procedures involve the addition of chemicals into wastewater treatment to form the precipitate with dye molecules and waiting for the insoluble particles to settle. Then the wastewater can be decanted to separate the sludge. The most common chemical precipitation method for dye removal is hydroxide precipitation. Chemical precipitation is an efficient method for the removal of dyes from wastewaters, but generation of sludge and high chemical cost are the major hurdle for the application of this technology at industrial scale (Ahmad et al., 2015).

Ozone oxidation

It is a very effective and fast decolorizing treatment, which can easily break the double bonds present in most of the dyes. Ozonation can also inhibit or destroy the foaming properties of residual surfactants and it can oxidize a significant portion of COD. Moreover, it can improve the biodegradability of those effluents which contain a high fraction of non-biodegradable and toxic components through the conversion (by a limited oxidation) of recalcitrant pollutants into more easily biodegradable intermediates (Ayeche, 2012). As a further advantage, the treatment does increase neither the volume of wastewater nor the sludge mass. Full scale applications are growing in number, mainly as final polishing treatment, generally requiring up-stream treatments such as at least filtration to reduce the suspended solids contents and improve the efficiency of decolorization

Sodium hypochlorite has been widely used in the past as oxidizing agent. In textile effluent it initiates and accelerates azo bond cleavage. The negative effect is the release of carcinogenic aromatic amines and other wise toxic molecules and, therefore, it should not be recommended (Karthik et al., 2014a).

Ion exchange

The ion exchange process is one of the most common techniques, which can effectively remove dyes from aqueous solutions through strong interactions between charged dyes and functional groups on ion exchange resins. This process involves the exchange of ions to form strong bonds between solutes and resins, thereby achieving effective separation. However, resins may be poisoned by unexpected constituents or rapidly exhausted by unexpectedly high loadings (Sharma, Saxena, & Gaur, 2014).

2.3.3. Biological method

Biological treatment procedures for the removal of contaminations from wastewater are considered highly useful due to their eco-friendly nature, minimum usage of chemicals and energy saving nature. The principle of the biological treatment procedures is the conversion of biodegradable wastes into simpler and harmless species through biological processes by various microorganisms. There are many types of biological treatment methods such as trickling filters, activated sludge process, anaerobic process, oxidation ponding etc. Biological process is cheaper than other methods (Karthik et al., 2014a). When compared to chemical methods, for biological process investment cost is 5-20 times less and operating costs are 3-10 times less than chemical methods [88]. However, conventional biological processes are not effective for treating dyestuff wastewater because many commercial dyestuffs are toxic to organism being used and result in the problems of sludge bulking, rising sludge and pin flock, most dyes are designed to resist to microbial attack, require large land area and less flexibility in design and operation (Monika, 2012).

2.4. Adsorption

Adsorption is a surface phenomenon in which adsorbate molecules or ions (liquid or gas) are concentrated on the surface of a solid. It is a process of binding molecules or particles onto the external surface of solid or internal surface, if the material is porous in a very thin layer (Kandasamy, Vigneswaran, Hoang, & Chaudhary, 2009). The binding to the solid are usually weak and reversible. The substance that accumulates at the interface is called ‘adsorbate’ and the solid on which adsorption occurs is known as ‘adsorbent’. Adsorption takes place primarily on the walls of the pores or at specific sites inside the particle. Separation occurs because of differences in molecular weight, shape or polarity, causes some molecules to be held more strongly on the surface than others. In many cases, the adsorbate is held strongly enough to allow complete removal of that component from the fluid. In the adsorption process, dye molecules may be adsorbed on the surface of an adsorbent through several forces such as hydrogen bonding, electrostatic interactions, van der Waals forces, hydrophobic interactions etc.

Generally, adsorption process is classified as physisorption and chemisorption (Kandasamy et al., 2009).

Physisorption is a type of adsorption in which the forces of attraction are intermolecular forces (van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation of vapors, and do not involve a significant change in the electronic orbital patterns of the species involved. The adsorbed molecules are not fixed to a specific site at the surface of adsorbent but are free to undergo translational movement within the interface. It is predominant at low temperature and is characterized by relatively low energy of adsorption.

Chemisorption is adsorption in which the forces involved are forces of the same kind as those operating in the formation of chemical compounds. Generally, adsorbents possess porous structures to increase the total exposed surface area and allow fluid to pass through faster (Samsami et al., 2020).

Adsorption process is an attractive and effective alternative treatment for dye removal from wastewater (Sun, Zhang, Wang, & Wu, 2013). There are many advantages of adsorption process, such as:

- Less land area (half or a quarter of what is required in a biological system),
- Lower sensitivity to diurnal variation,
- Toxic chemicals do not affect the process,
- Greater flexibility in the design and operation,
- Superior removal of organic contaminants,
- High dye removal efficiency,
- Dose not form harmful substances, and
- Easy of operation

2.4.1. Factors affecting adsorption process

The initial dye concentration, solution pH, contact time and adsorbent dosage are usually the main factors that govern the performance of most of the adsorption process.

Optimization of such conditions will greatly help in the development of industrial-scale dye removal treatment process. Some of the factors affecting adsorption of dyes are discussed below.

Effect of dye concentration

The amount of adsorption for dye removal is highly dependent on the initial dye concentration. The effect of initial dye concentration depends on the immediate relation between the concentration of the dye and the available sites on an adsorbent surface. In general, the percentage of dye removal decreases with an increase in the initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface. On the other hand, the increase in initial dye concentration will cause an increase in the capacity of the adsorbent and this may be due to the high driving force for mass transfer at a high initial dye concentration (Yagub et al., 2014).

Effect of contact time

The contact time between the pollutant and the adsorbent is a significant importance in the wastewater treatment by adsorption. A rapid uptake of pollutants and establishment of equilibrium in a short period signifies the efficiency of that adsorbent for its use in wastewater treatment. In physical adsorption most of the adsorbate species are adsorbed within a short interval of contact time. However, strong chemical binding of the adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. Available adsorption studies in literature reveal that the uptake of adsorbate species is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be nearly constant. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases (Nasr, Hamdi, & Elhalouani, 2017).

Effect of adsorbent dose

Adsorbent dosage is an important process parameter to determine the capacity of an adsorbent for a given amount of the adsorbent at the operating conditions. Generally, removal efficiency increases with increasing adsorbent dosage, where the quantity of sorption sites at the surface of adsorbent will increase by increasing the amount of the adsorbent. The effect of adsorbent dosage gives an idea for the ability of a dye sorption to be adsorbed with the smallest amount of adsorbent, to recognize the capability of the adsorbent from an economical point of view (Sartape et al., 2017).

Effect of solution pH

Another important factor affecting the capacity of adsorbent in dye removal is solution pH. The efficiency of adsorption is dependent on the solution pH, since variation in pH leads to the variation in the degree of ionization of the adsorptive molecule and the surface properties of adsorbent (Yagub et al., 2014). pH value of the solution will determine the surface charge of the adsorbent which will affect the interaction between the adsorbate and adsorbent. There are two possible mechanisms for the effect of pH on adsorption of dyes on any adsorbent: electrostatic interaction between the protonated or deprotonated groups of adsorbents with dyes, and the chemical reaction between the adsorbate and the adsorbent. The hydrogen ion and hydroxyl ions are adsorbed quite strongly, and therefore, the adsorption of other ions is affected by the pH of the solution. The change of pH affects the adsorptive process through dissociation of functional groups on the active sites of the adsorbent. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of the adsorption process. It is a common observation that the surface adsorbs anions favorably at lower pH due to presence of H^+ ions, whereas, the surface is active for the adsorption of cations at higher pH due to the deposition of OH^- ions (Kheddo, Rhyman, Elzagheid, Jeetah, & Ramasami, 2020).

2.5. Adsorption isotherm models

Equilibrium study on adsorption provides information on the capacity of the adsorbent. An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants. It is the relationship that shows the distribution of adsorbate between the adsorbed phase and the solution phase at equilibrium (Yunusa & Ibrahim, 2019). If the adsorbent and adsorbate are contacted long enough, equilibrium will be established between the amount of adsorbate adsorbed and the amount of adsorbate in solution. The equilibrium relationship is described by adsorption isotherms. Equilibrium data can be analyzed using commonly known adsorption systems. Several mathematical models can be used to describe experimental data of adsorption isotherms. The most commonly used isotherms are the Langmuir and Freundlich isotherms.

2.5.1. Langmuir isotherm model

Langmuir adsorption isotherm is one of the most popular isotherms for the removal of heavy metals, dyes, organic pollutant by adsorption onto activated carbon, clay, agricultural waste, industrial waste, etc. It is valid for monolayer adsorption on specific homogenous sites containing a finite number of identical sites (Yunusa & Ibrahim, 2019). The basic assumptions underlying Langmuir's model which is also called the ideal localized monolayer model are that the molecules are adsorbed on definite sites on the surface of the adsorbent and each site can accommodate only one molecule (monolayer). The area of site is fixed, quantity determined solely by the geometry of the surface, and the adsorption energy is the same at all sites. In addition, the adsorbed molecules cannot migrate across the surface or interact with neighboring molecules. The Langmuir isotherm model estimates the maximum adsorption capacity produced from the complete monolayer coverage on the adsorbent surface. Based upon the above assumptions, Langmuir isotherm model equation can be represented by equation 2.1(Ramachandran, Vairamuthu, & Ponnusamy, 2011).

Langmuir

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \qquad \ldots\ldots 2.1$$

Adsorption parameters were determined by transforming the above equation into linear form.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \qquad \ldots\ldots 2.2$$

Where:

q_e= amount of dye adsorbed per gram of the adsorbent at equilibrium (mg/g).

q_m= maximum monolayer coverage capacity (mg/g)

C_e= equilibrium concentration of adsorbate (mg/L)

k_L= Langmuir isotherm constant (L/mg)

The values q_m and K_L can be computed from the slope and intercept of the Langmuir plot of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant referred to as separation factor or equilibrium parameter (Y. Zhang et al., 2019).

$$R_{L=}\frac{1}{1+(1+K_L C_0}\text{……………………………………………………………...2.3}$$

Where:

R_L= Langmuir equilibrium parameter

C_0 = initial concentration (mg/L)

K_L = constant related to the energy of adsorption, Langmuir Constant (L/mg)

RL value indicates the adsorption nature to be either unfavorable if R_L>1, linear if R_L=1, favorable if 0< R_L<1 and irreversible if R_L=0.

2.5.2. Freundlich isotherm model

Freundlich isotherm model assumes that the adsorption occurs on a heterogeneous surface and non-uniform distribution of the heat of adsorption over the adsorbent surface takes place (Yunusa & Ibrahim, 2019). Freundlich equation suggests multilayer adsorption and the sorption energy exponentially decreased on completion of the sorption centers of an adsorbent. It is assumed that the stronger binding sites are initially occupied with the binding strength decreasing with increasing degree of site occupation (Sun et al., 2013).

The linearized form of Freundlich model is expressed as follows:

$$\log q_e = \log k_f + {}^{1}/_{n} \log c_e \text{…………………………………………………………2.4}$$

Where:

$q_{e=}$Amount of dye adsorbed per gram of the adsorbent at equilibrium (mg/g)

C_e = Equilibrium concentration of adsorbate (mg/L)

K_f = Freundlich isotherm constant (mg/g)

n = Adsorption intensity

The equilibrium adsorption capacity, q_e (mg/g) can be calculated using the mass balance equation given (Sartape et al., 2017).

$$q_e = v\frac{(C_0 - C_e)}{w} \qquad \text{2.7}$$

Where c_0 and c_e are the initial and final equilibrium concentration of adsorbate (mg/L), V is volume of the solution (L) and W is the dry adsorbent (g).

The amount of adsorbate adsorbed, q_t (mg/g) at any time can be calculated using Equation below.

$$q_t = v\frac{(C_0 - C_t)}{w} \qquad \text{2.8}$$

Where, c_t is the concentration of adsorbate, (mg/L) at any time.

The percentage removal of adsorbate can be calculated using the following relationship (Abdulabbas et al., 2020).

$$\%\text{Removal of MB} = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad \text{2.9}$$

Where c_0 and c_e are the initial and final equilibrium concentration of adsorbate (mg/L). The applicability of two adsorption isotherm (Langmuir and Freundlich) can be compared by evaluating the multiple regression correlation coefficients, R^2. In regression, the R^2 coefficient of determination is a statistical measure of how well the regression line approximates the real data points. R^2 is a number between zero and one that would give some information about the best fit of a model. If the value of R^2 close to zero suggests a poor model. If the value of R^2 is 1.0 indicates that the regression line perfectly fits the data. If the Value of R^2 occurs outside the range 0 to 1, it is used to measure the agreement between observed and modeled value (Fu et al., 2018).

2.6. Adsorption kinetics models

The dynamics of the adsorption can be studied by the kinetics of adsorption in terms of the order of the rate constant. The adsorption rate is an important factor for a better choice of material to be used as an adsorbent; where the adsorbent should have a large adsorption capacity and a fast adsorption rate. Most of adsorption studies used Pseudo-first-order and Pseudo-second-order models to study the adsorption kinetics (Kheddo et al., 2020).

2.6.1. Pseudo first-order kinetics model

Pseudo first-order kinetics model is one of the most widely used rate equation to describe the adsorption of adsorbate from the liquid phase. The linear form of pseudo first-order rate is given in equation 2.8(Ramachandran et al., 2011).

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \qquad \text{...2.10}$$

Where: q_e and q_t = adsorption capacity at equilibrium and at time t, respectively (mg/g)

K_1 = rate constant of pseudo first-order kinetics (min^{-1})

The plot of $\log(q_e - q_t)$versus t should give a linear relationship from which K_1 and $q_e$can be determined from the slop and intercept of the plot, respectively.

2.6.2. Pseudo second-order kinetics model

The adsorption kinetics was also described as pseudo-second order kinetics using equation 2.11.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right) t \qquad \text{...2.11}$$

Where: q_e and q_t= adsorption capacities at equilibrium and at time t, respectively (mg/g)

K_2 = rate constant of pseudo-second-order sorption (g/mg/min)

If Pseudo-second order kinetics is applicable, the plot of $\frac{t}{q_t}$ against t should give a linear relationship, from which q_e and K_2can be determined from the slope and intercept of the plot (Zhang et al., 2016).

3. MATERIAL AND METHOD

3.1. Chemicals and Reagents

All the reagents and chemicals used in this study were analytical grade. Deionized water for rinse equipments, 37% v/v Hydrochloric Acid and Sodium Hydro Oxide pellet for pH adjustment, Ethanol also used for rinse equipments, methylene blue ($C_{16}H_{18}N_3SCl$) for stock solution preparation.

3.2. Equipment and Apparatus

The apparatus used were UV-Vis spectrophotometer (Sm 1600 spectrophotometer; Hyderabad500018,India), furnace (SX-2.5-12, China), Model SX-2f.12), Fourier Transform Infrared Spectroscopy(FTIR) (FT/IR-6600 FTIR Spectrometer, JASCO United States), X-ray diffraction (XRD) (XRD-7000-X-RAY Diffractometer ; SHIMADZU Japan), Scanning Electron microscope (SEM) (JEOL JCM-6000plus model instrument), DTA-TGA instrument (DTG-60H, Shimadzu Co., South Korea), Magnetic stirrer (PMC 502P United States), air tight polythene container, pH meter, digital balance (GF 6100 ,AND company Tokyo Japan), Universal drying Oven (SHIVKI-PID-906), and sieving equipment (Arm field, CEN-MKII-OOA). The glass wares used were volumetric flask, Filter paper, vacuum desiccators, beaker, conical flask, micropipettes and burette.

3.3. Sample Collection

The materials that were utilized for this study in making ceramsite were bentonite, dewatered sewage sludge, and bagasse fly ash. The sewage sludge used was obtained from wastewater treatment plant of Adama Science and Technology University. Bagasse fly ash, a waste material of sugar industry, was collected from Wonji sugar factory. Bentonite was received from Afar Region (Gewane area) in north eastern part of Ethiopia.

3.4. Preparation of the Adsorbent

The sewage sludge, Bagasse fly ash, and Bentonite were washed with distilled water to remove dust, dirt, clay and other non-bagasse. DSS, Bagasse fly ash, and bentonites (40, 30, 40g) respectively were dried at 105^{o}C for 24 h to remove moisture and then ground in a planetary mill for 40min. The ground products were passed through a 0.15 mm sieve and collected for further experiments (G. Cheng et al., 2018). Then based ceramsite was prepared by mixing DSS, bagasse fly ash, and bentonite in ratio of weight (4:3:4) respectively. Then the sample mixed was transferred into a muffle furnace and then preheated at the preheating temperature of 250^{o}C for 20min. and then based TGA result sintered (calcinated) at a sintering temperature of 600^{o}C and for the sintering time of 30 minute. After sintering, the ceramsite was cooled to room temperature for 120 min. and then stored in an air tight container for future use (K. Wu, Hu, Zhang, Xu, & Yang, 2022).

3.5. Characterization of the adsorbent

3.5.1. Physico-chemical analysis of Ceramsite

The prepared ceramsite was characterized for physic-chemical parameters such as pH, moisture content, ash content, Bulk density, Particle density and porosity. An ASTM (D1102-56) standard procedure was followed to determine the physic-chemical parameters of the ceramsite (Rhaman, Haque, Rouf, Siddique, & Islam, 2015). The procedures of physic-chemical parameters determination are described below.

pH

pH of ceramsite prepared from sewage sludge, bagasse ash and bentonite were measured by adding 1.0 g ceramsite to 100 mL distilled water in a 250 mL beaker volume then the beaker was covered with a watch glass and boiled on the hot plate for 5 min and sample was allowed to stabilize and then pH was measured using an electronic pH meter (Jin, Du, Zheng, & Zhang, 2016).

Determination of moisture content

A crucible was taken and weighed. 2g of sample was added in the crucible and weighed. It was kept in hot air oven at 105°C for 24h. It was taken out and kept in the desiccators. Then the weight was measured and the moisture content is calculated as:

$$M = \frac{M_2 - M_3}{M_2 - M_1} \times 100\% \quad \text{......3.2}$$

Where, M = moisture content (%), M_2= mass of crucible plus sample (84.401g), M_3 = mass of crucible plus dried sample (84.288g), M_1 = mass of empty crucible (82.4g). Accordingly, moisture content is calculated to be 5.63%.

Determination of ash content

9.66 g of sample was taken in crucible and weighed. The sample was kept in a muffle furnace for 2h. at a temperature of 550°C. Then, it was taken out and kept in desiccators for half an hour to cool down. Then, again the weight was measured and ash content was calculated as:

$$A = \frac{M_2 - M_0}{M_1 - M_0} \times 100\% \quad \text{.........} 3.1$$

Where, A = Ash content, M_1= Mass of crucible plus sample (95.876g), =M_2 mass of crucible plus ash sample (after heating) 91.5748g, M_0 = mass of empty crucible (86.219g). So, ash content is calculated to be 55.46%.

Bulk density

The sample was dried to constant weight for 24 hours in hot air oven at 105^{o}C. 71.4 gm of the dried sample was transferred to 100mL graduated cylinder carefully using funnel. Then, the cylinder was tapped three times to settle the ceramsite. The volume was read and the bulk density was calculated as;

$$Bd = \frac{M}{P} \quad \text{.........} 3.3$$

Where, B = Bulk density (gm/cm3), M = Mass of dry sample (67.4gm), P =Volume of packed sample 100cm^3. So, bulk density is calculated to be 0.674gm/cm3.

Particle Density

60mL distilled water was measured and transferred to 100mL Cylinder. 67.4gm of dried sample was weighed and transferred into the cylinder with water, then, it was stirred to remove trapped air. The volume was read and the particle density was calculated as;

$$\mathrm{Pd} = \frac{\mathrm{M}}{\mathrm{S}} \quad \text{..........} \quad 3.4$$

Where, P =Particle density (gm/cm3), M = Mass of dry sample (67.4gm), S=Volume of sample 32cm^3. So, particle density is calculated to be 2.106gm/cm3.

Porosity

Porosity is the fraction of the total powder volume that is taken up by the pore. The porosity of the ceramsite powder was determined based on the particle density and bulk density of the ceramsite. The porosity for the ceramsite powder was obtained from bulk and particle density using equation 3.5:

$$\mathrm{P} = 1 - \left(\frac{\mathrm{Bd}}{\mathrm{Pd}}\right) \times 100\% \quad \text{..........} \quad 3.5$$

Where, P= Porosity (%), Bd= Bulk density, Pd=Particle density, so porosity is calculated to be 67.99%.

3.5.2. Characterization

i) Thermogravimetric Analysis -Differential Thermal Analysis (TGA-DTA) Analysis

The thermal property of ceramsite were conducted in order to decide the calcination temperature and to study thermal stability of ceramsite using differential thermogravimetric analysis (TGA) coupled with Differential Thermal Analysis (DTA) (Shimadzu co., DTG-60H, South Korea Japan). An oven-dried ceramsite samples were heated from room temperature to 1200°C in a Platinum/alumina cup with a heating rate of 10 °C/min, and an empty Platinum/alumina cup was used as control.

ii) Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis of the ceramsite was done before and after adsorption at Bahir Dar University. Pellets were prepared by adding 1 mg of sample with about 300 mg of KBr in an agate mortar, and then the mixture is pressed at a pressure of 12 Pa for about 3 min and the pellet adsorbent sample was scanned over the range 500-4,000 cm-1 to determine the availability of the functional groups on the surface of ceramsite (Ravulapalli & Kunta, 2018).

iii) Scanning electron microscopy

The surface morphology of ceramasite before and after adsorption was investigated using a scanning Electron Microscope JEOL (JCM-6000plus model instrument) and the SEM images were noted from different areas of adsorbent at 10.0KV at varying resolution from 150x to 10,000x.

iv) X-Ray Diffraction (XRD) Analysis

The ceramsite prepared was characterized before and after adsorption by x- ray diffraction (XRD-7000-X-RAY Diffractometer) at Adama Science and Technology University, Material science department. A one gram of fine powder ceramsite was packed with standard sample holder and XRD spectrum of the sample was recorded from 10^0- 80^0 with 2θ angles using Cu kα radiation (λ=1.54 Å) source operating at voltage 40kv and current 30 within scanning speed of 4 (deg/min).

3.6. Methylene Blue (MB) adsorption study

3.6.1. Batch adsorption experiment

Batch adsorption experiment was performed by contacting a certain concentration of dye with the ceramsite at specified process conditions. For this set of experiments, a 1000 mg/L equimolar stock solution of MB was first prepared and the needed concentrations were diluted from it in 250 ml volumetric flask. The pH of the solution was adjusted by using 0.1 M HCl and 0.1 M NaOH to bring to the required pH. The appropriate concentration of the methylene blue was mixed with the ceramsite and stirred for different times. The solution obtained after adsorption was filtered to separate the adsorbent from the supernatant. The supernatant is then measured for its remaining concentration using a UV/Vis spectrophotometer. The values of percentage removal and amount of MB adsorbed at equilibrium q_e (mg/g) were then calculated using the Langmuir and Freundlich isotherm models. The effects of various parameters such as dye initial concentration, contact time, pH, and adsorbent dosage were studied.

3.6.2. Analysis of MB dye concentration using UV/Vis spectrophotometer

To measure the concentration of MB in aqueous solution using UV/Vis spectrophotometer, a calibration curve was needed to be set up. The calibration curve is constructed by preparing orderly increasing concentration solutions and measuring the absorbance of this solution. MB absorbs UV/Vis light at a wavelength of 665 nm. An absorbance versus concentration linear graph was drawn and equation of the straight line was determined. So, samples from the absorption studies are brought and their absorbance measured. The concentration of the solutions was then determined from the calibration graph.

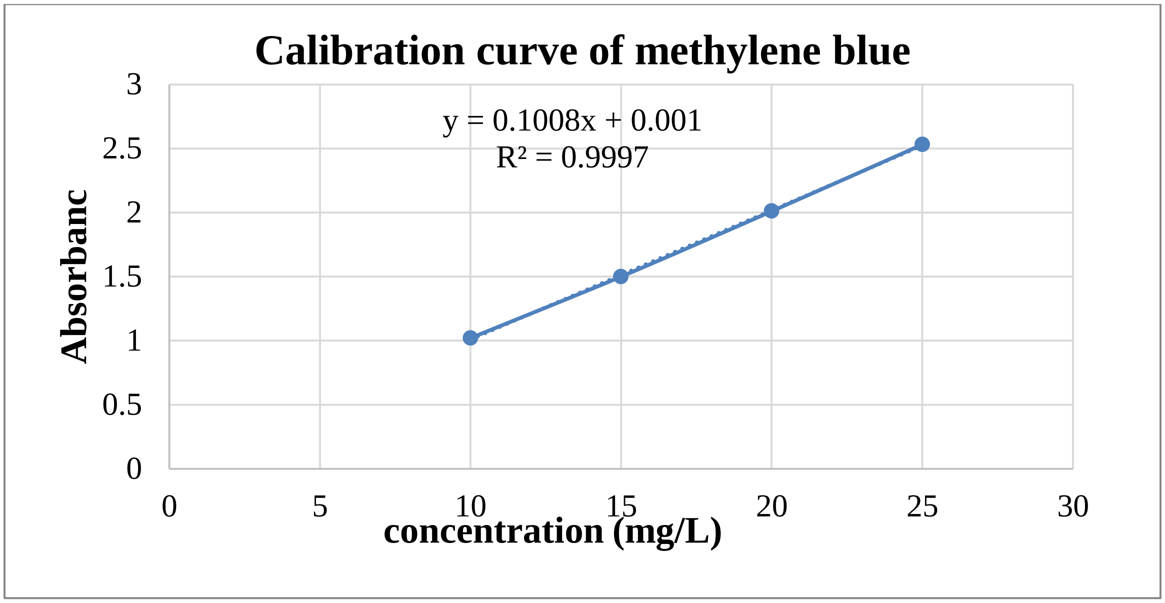


Figure 3.1: Calibration line for determination of methylene blue dye.

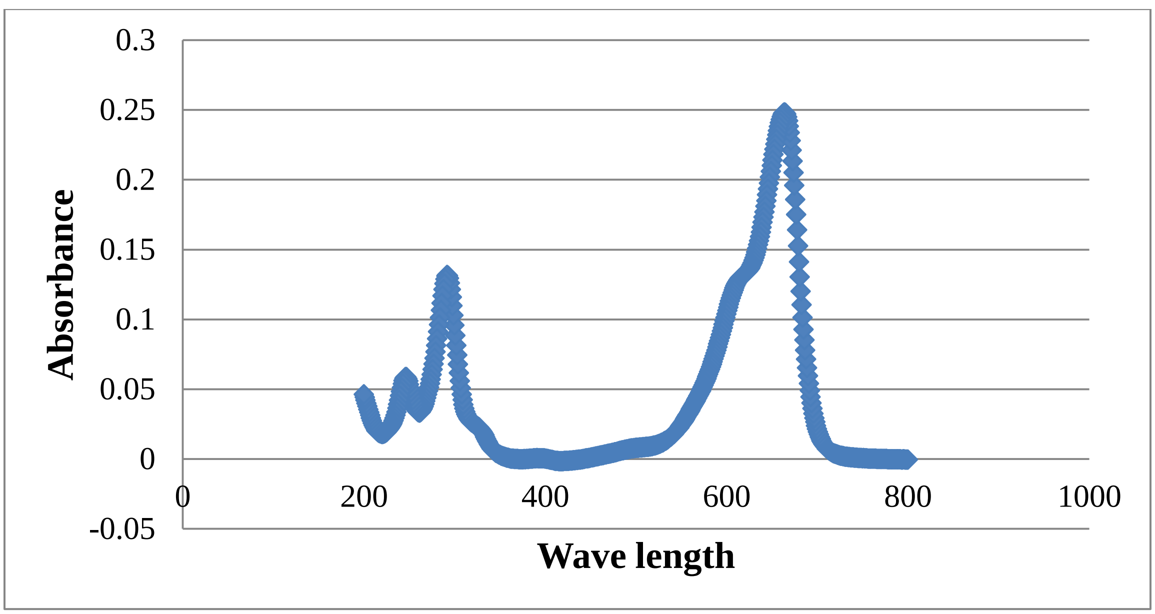


Figure 3.2: UV/Vis light spectrum of MB dye.

3.6.3. Adsorption performance study

Various adsorption experiments were carried out to investigate the effects of the factors that influence the adsorption process.

The test was done by taking weighed dosage 0.1, 0.2, 0.3, 0.4 and 0.5gm of the adsorbent in 50mL of adsorbates and at pH of2,4, 6, 8and 10 and 50mLof 10, 20, 30, and 50 mg/l initial concentration of methylene blue solution with the contact time 30, 60, 90 and 120 min. The pH of solution was adjusted by adding 0.1M HCl and 0.1M NaOH solution until pH reach to desired pH. The solutions were stirred at room temperature (25℃) for about the desired time. The samples were then filtered (gravitational filtration) using a Whatman filter paper (125mm)and the filtrate was analyzed for the residual methylene blue concentration in the solution. Equilibrium of this experiment was studied using Langmuir, and Freundlich, isotherm models. The kinetics was also studied by Pseudo- first order and Pseudo-second order models. Satisfactory conformity between experimental data and the model-predicted values was expressed by the correlation coefficient (R^2).

Finally, the adsorption capacity and removal efficiency of ceramsite (adsorbent) were determined for all samples as follows. Methylene blue concentration retained in the adsorbent can be calculated as: -

$$q_e = v\frac{(Co-Ce)}{w} \qquad \text{……………………………………………………………3.3}$$

Percentage removal efficiency can be calculated as:

$$\%\text{removal of MB} = \frac{(Co-Ce)}{Co} \times 100 \qquad \text{………………………………………………3.4}$$

Where: Co and Ce = initial and equilibrium concentrations (mg/L) of the dye in solution respectively

v= volume of the solution (L)

w= mass of dry adsorbent used (g).

3.7. Adsorption Isotherm

To study the adsorption isotherms the optimum conditions which were found from previous optimization experiments was applied only by varying initial MB dye concentration. These experiments were carried out using initial MB dye concentration in the range of 10mg/L-50mg/L with 10mg/L difference. For each initial MB dye concentration 50mL of sample was taken at optimum agitation, optimum adsorbent dose and room temperature for 90 min. The data from the experiment were fitted into Langmuir and Freundlich adsorption isotherm models.

3.8. Kinetics Study

It is very important to know the rate at which the process takes place and the factors that control the rate of the process, for this purpose kinetics of the process was evaluated. These experiments were conducted for the optimum contact time by setting MB dye concentration, pH, adsorbent dose and agitation speed constant. Then sample was withdrawn in every 30 minute interval for determination of residual MB dye concentration in the solution. Then data from the experiment was introduced into Pseudo- first order and Pseudo-second order models.

3.9. Reusability Experiment

To study the regeneration and reusability of the adsorbent, batch adsorption experiments were conducted with adsorbent dosage of 0.5 g and initial dye concentration of 10mg/L at room temperature with a stirring rate of 150 rpm. The adsorbent was recovered after the experiment through centrifugation and filtration, followed by washing with 0.1NaOH and distilled water and dried. Same procedure was repeated 3 times (Santhi, Manonmani, Smitha, & Mahalakshmi, 2009).

3.10. Data analysis and interpretation

All data generated from the above experiments will be analyzed using the Microsoft Excel, Window program and the linear regression values will be computed as required.

4. RESULT AND DISSCUSION

4.1. Characteristics of ceramsite

4.1.1 Physico-chemical Analysis of ceramsite.

As shown in Table 4.1, the ceramsite prepared has a moisture content of 5.6 %, has a pH of 6.8 and has ash content of 55.46. The ceramsite has lower moisture content as compared to other adsorbents such as activated carbon from coffee husk where the moisture content was 19% (Berihun & Solomon, 2018). This indicates that the prepared ceramsite may have higher adsorption efficiency since water molecules can have the potential effect in the pores of an adsorbent through filling the adsorbent binding site before it contact with the solution. Therefore, adsorption efficiency decreased with an increase in moisture content of an adsorbent (Berihun & Solomon, 2018). Ash content has an influential role in affecting the quality of ceramsite produced. The presence of excessive ash can lead to clogging of the pores on the ceramsite so that the surface area of cermasite becomes reduce. The ceramsite has lower ash content as compared to other adsorbents such as activated carbon from coffee husk (Berihun, 2017). This indicates that the prepared ceramsite may have higher adsorption efficiency. Nearly neutral pH of the ceramsite confirmed that this will pose no problem and does not require evaluation of acid leaching of inherent chemical elements (Wei, Chen, & Wang, 2016). Ceramsite prepared has a bulk density of 0.674, Particle density of 2.106 and the porosity value of 67.99%. The bulk density and particle of ceramsite has low, and the porosity becomes high. This indicated that the ceramsite body is less dense and it may have relatively large potential of adsorbing capacity (Singh, Chauhan, Jain, & Sharma, 2017).

Table 4.1: physico-chemical analysis of ceramsite prepared from sewage sludge, bagasse ash and bentonite.

Contents	Value
Moisture content (%)	5.63
Ash value (%)	55.46
Ph	6.8
Bulk density (g/cm^3)	0.674
Particle density (g/cm^3)	2.106
Porosity (g/cm^3)	67.99

4.1.2 TGA-DTA Analysis

The Differential Thermal Analysis (DTA) and Thermogravimetry Analysis (TGA) results of ceramsite that shows the changes in materials that are caused by heat /thermal properties/ were shown in Figure 4.1. As shown in the TGA curve, the ceramsite mass change below 250°C was nearly 3.31% , which was considered as the pre-heating temperature of the ceramsite prepared , while a drastic decline occurred within 250–600 °C and mass change 37.02%, and above 600°C little ceramsite was residual (15.99%). After temperature of 600°C, TGA curve became almost constant. We can confirm this one from weight loss information from the TGA curve. The weight loss information was studied from the TGA thermograph. The first weight loss takes place due to the OH groups present at the surface, so water molecules have been removed. The second weight is due to the formation of a completely pure ceramsite phase. The temperature beyond which the weight loss is constant is used as the calcination temperature of ceramsite (Franus, Barnat-Hunek, & Wdowin, 2016). Therefore, Calcination was performed at 600°C to remove unwanted remnants of the raw materials (sewage sludge, bagasse ash and bentonite), and improve the purity of ceramsite.

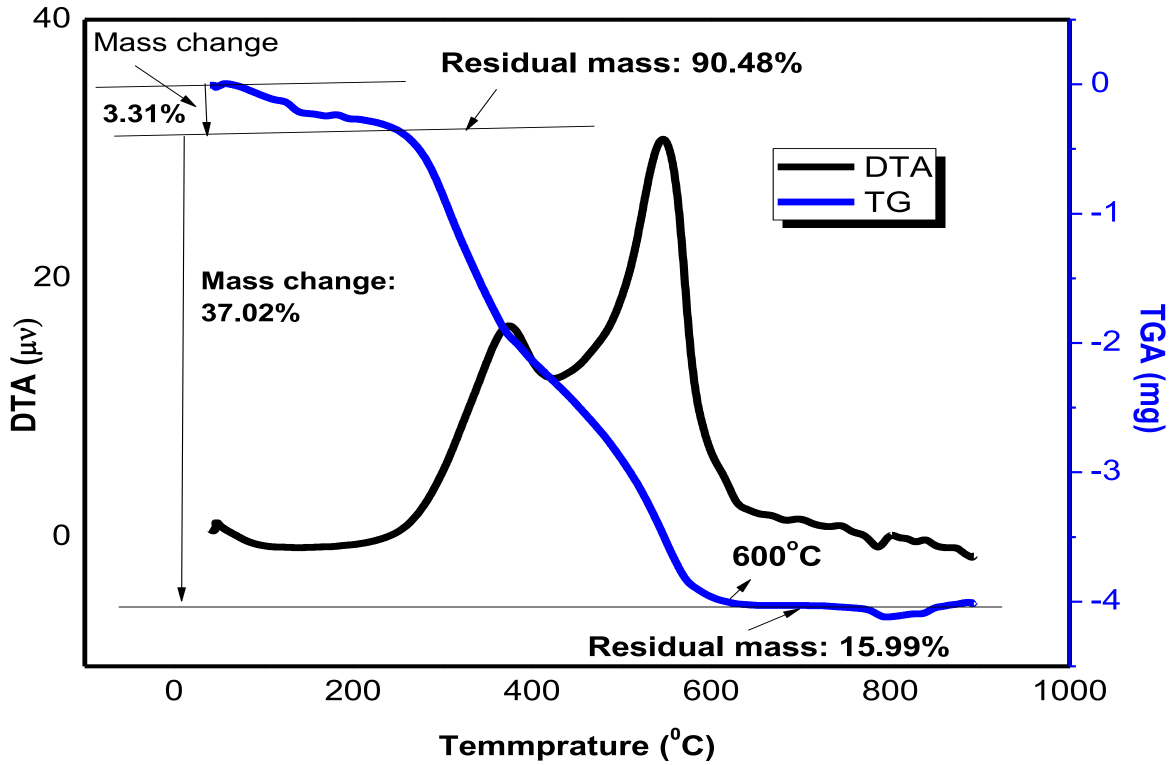


Figure 4.1 The Differential Thermal Analysis (DTA) and Thermogravimetry Analysis (TGA) analysis results of uncalcined ceramsite.

4.1.3 XRD Analysis

Figure 4.2 illustrates the X-ray diffractogram (XRD) pattern of the ceramsite before and after adsorption of MB dye. The X-ray diffraction analysis was performed to establish the inorganic crystalline composition of ceramsite. The XRD spectrum of the ceramsite confirmed the presence of calcite, hematite, alumina, illite, kaolite, quartz, montomorollonite, vivianite minerals. In comparison with the XRD result reported on bentonite, sewage sludge and bagasse ash, Quartz and calcite are found to be the main component of ceramsite (Patowary, Patowary, Kalita, & Deka, 2016); (Franus et al., 2016). The presence of diffraction peak corresponding to angle (20.46º) confirmed the presence of montmorillonite in the samples. The data also showed the presence of minerals such as calcite (24.78, 30.8, 32.78, 39.6, 41.92, 47.64, 48.64º), alumina (27.98 and 43.34º), vivianite (15.96º), Hematite (24.36 and 35.6º), illite (37.26º), kaolinite (67.52º) and quartz (21.28, 26.18and 29.46º) in ceramsite prepared from sewage sludge, bagasse ash and bentonite. In which, their intensity in the XRD pattern clearly indicated the ceramsite contained quartz and calcite as the major crystalline phase and the illite, Kaolinite and montmorillonite clay minerals as the minor phase. The observed intense diffraction peaks of quartz and calcite in the XRD pattern of ceramsite after heat treatment is due to they are remained intact at the calcination temperatures of 600 °C (Ayele, Pérez-Pariente, Chebude, & Díaz, 2016). The XRD patterns of were also in agreement with the TGA-DTA analysis result obtained from TGA-DTA (fig.4.1). The XRD pattern of ceramsite before and after adsorption is depicted in Figure 4.2, and additionally, no obvious change is observed in the XRD pattern after adsorption indicates its great stability for MB adsorption in aqueous solutions.

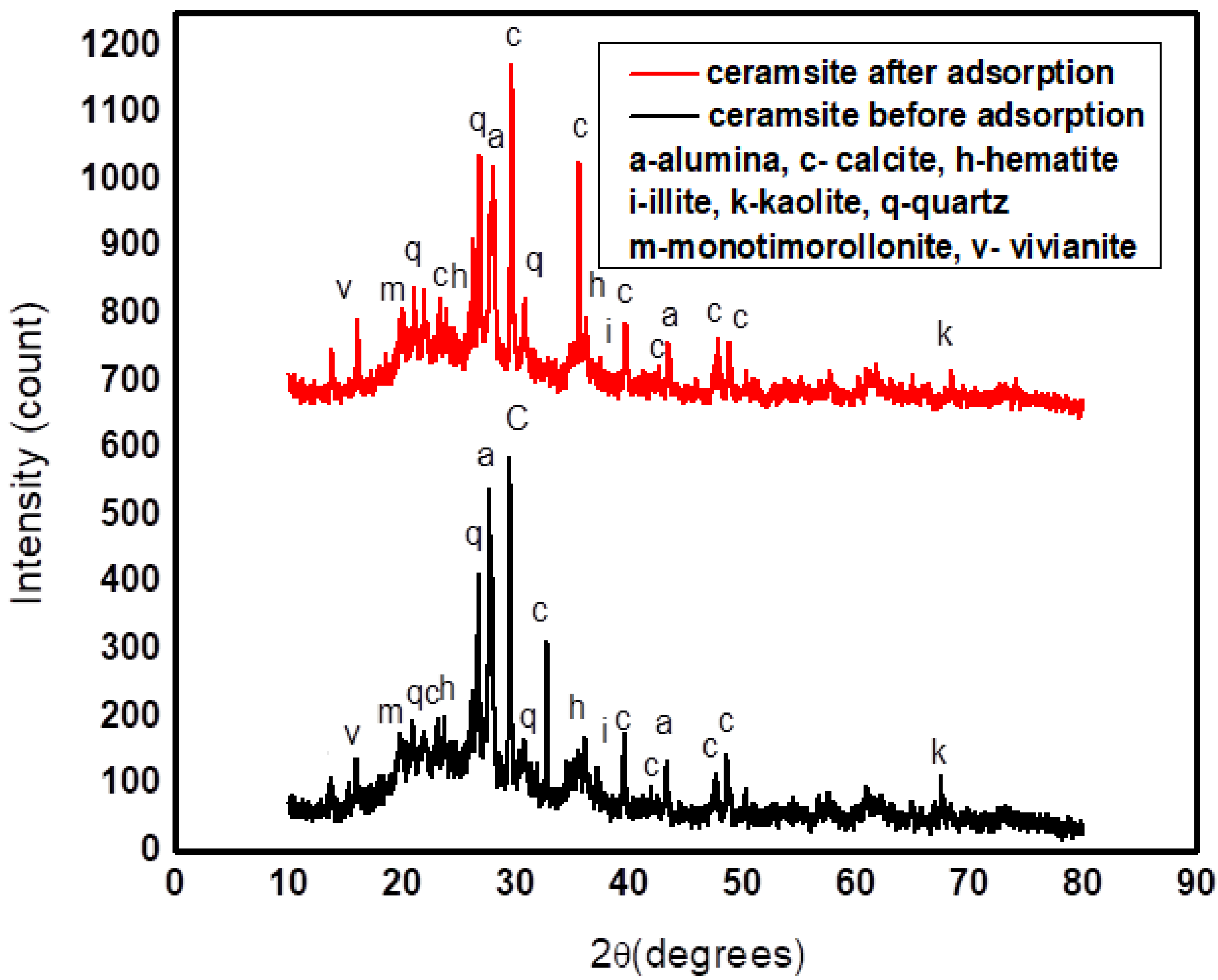


Figure 4.2 XRD spectrum of ceramsite before and after adsorption of methylene blue dye.

4.1.3 FTIR Analysis

The FT-IR spectra of ceramsite measured between wave number ranges 400-4000 cm^{-1} before and after MB dye sorption were shown in figure 4.3. It is measured to detect changes in the vibration frequencies of the functional groups after and before adsorption.

Absorption bands in the region between 3100 and 3400 cm-1 indicates the presence of both free and hydrogen bonded OH groups on the adsorbent surface. This stretching is due to both the silanol (Si–OH) groups and adsorbed water (peak at 3436 cm^{-1}) on the surface, while bending vibration at 1635 cm^{-1}. Si-O and Al-O stretching modes are found in the 1200-700 cm-1 range, while Si-O and Al-O bending modes dominate in the 600-400 cm-1 region (De Castro et al., 2018). The peak around 1017 cm^{-1} is related with the stretching vibrations of Si-O groups, while the bands in the wave number range of 400–500 cm^{-1} is ascribed to the bending vibrations of O–Si–O and O–Si–O- (Y. Li, Huang, Xu, Ma, & Guo, 2020). Some distinct changes are observed between the spectra before and after methylene blue adsorption on ceramsite. In the case of the spectrum obtained after the adsorption of methylene blue, there is a remarkable change of the positions of infrared bands with no change intensities. The changes in the FTIR spectra, the results confirmed that the process involved is type inclusion of methylene blue with functional groups present in the ceramsite.

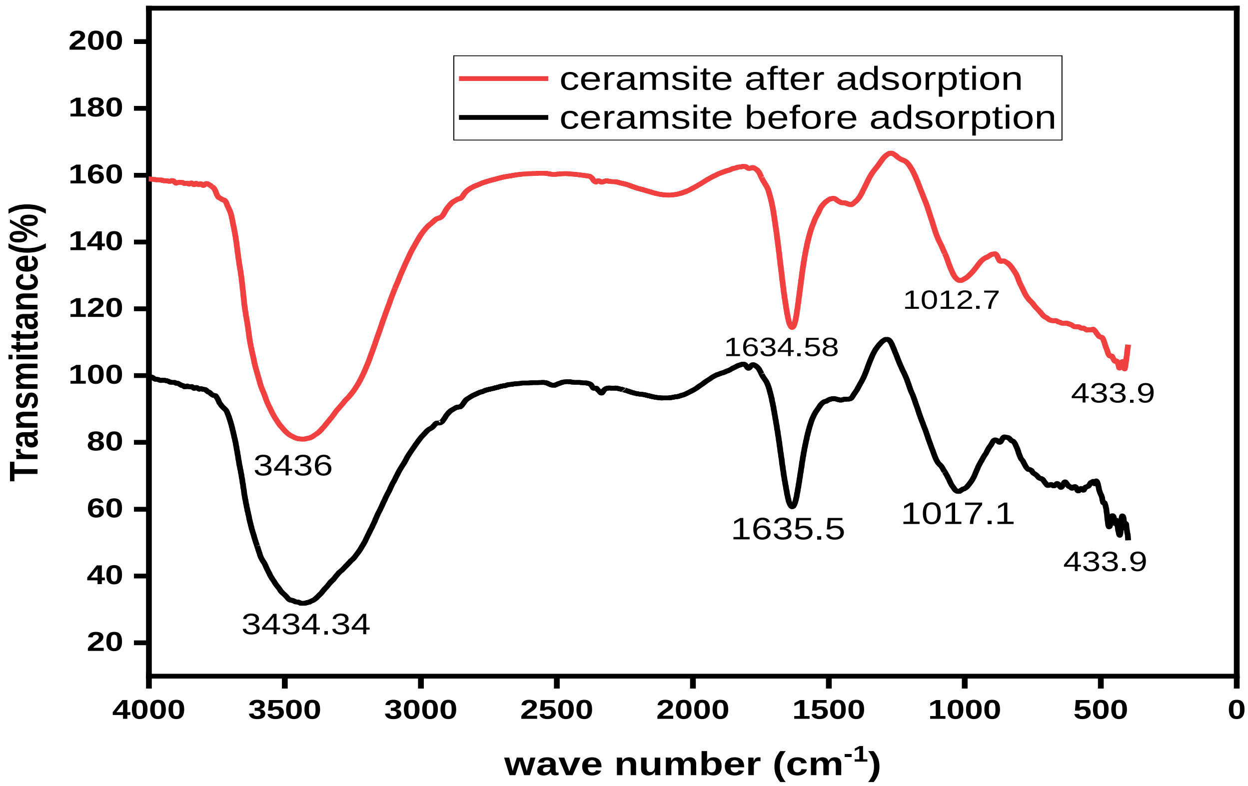


Figure 4.3 FTIR spectra of Ceramsite before and after adsorption of methylene blue.

4.1.4 SEM Analysis

Differences in SEM micrographs were observed between surface topography of ceramsite derived from sewage sludge, bagasse ash and benotonite before and after adsorption. The micrographs before and after adsorption of methylene blue on the surface of the adsorbent material are given in Figure 4.4. The SEM image of the adsorbent before adsorption shows unoccupied pore of various sizes and shapes on the adsorbent shown in Figure 4.4 A. These features favor the easy penetration of the adsorbate onto the surface of the adsorbent but after adsorption there is an emphatic change such as reduction in the size of some pores, disappearance of some pores, disappearance of corners or edges. As seen in Figure 4.4 B the outer pores are covered by adsorbents and the pores are no longer visible.

These reveal that the adsorption of methylene blue on the surface of the ceramsite derived from sewage sludge, bagasse ash and benotonite.

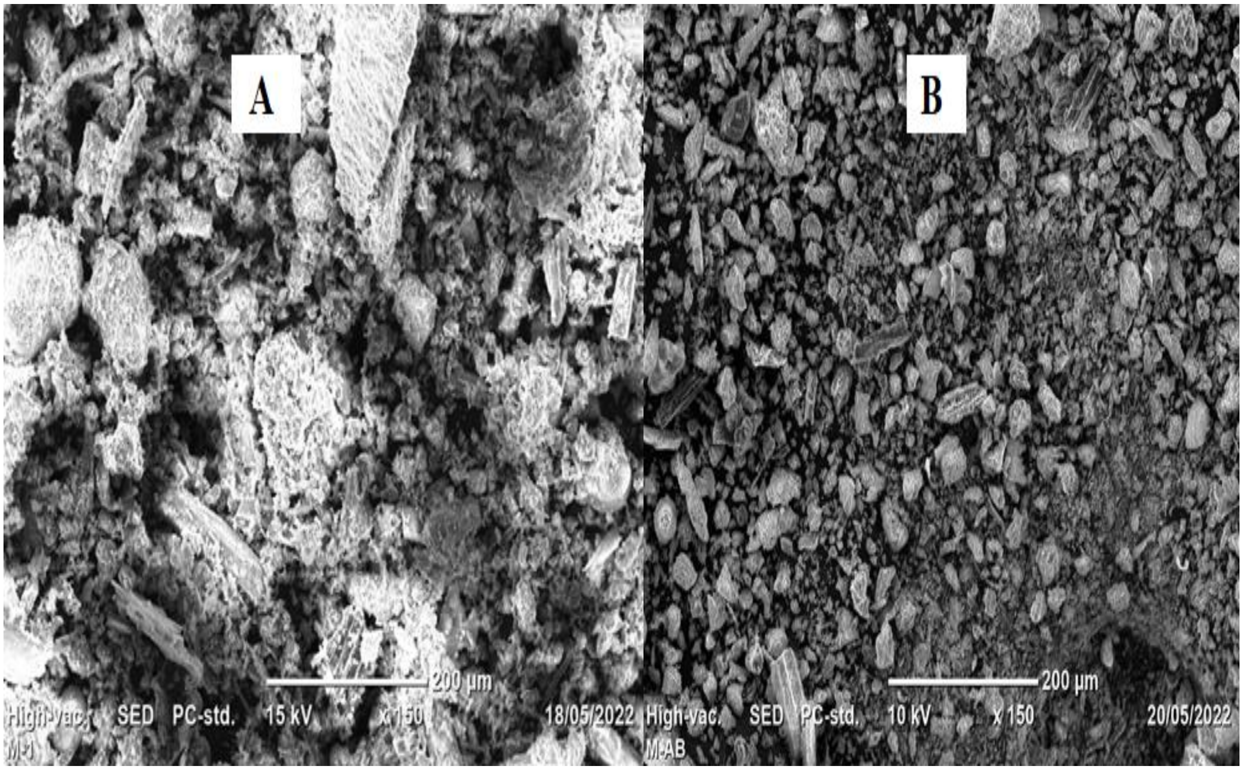


Figure 4.4 Scanning Electron Microscopy (SEM) image of cemasite before (A) and after (B) adsorption of MB dye.

4.2 Effect of Adsorption Parameters

4.2.1 Effect of pH

The pH of the solution has played a significant role on adsorption of MB on the surface of ceramsite in the pH range of 2-10, as shown in Fig. 4.6. The methylene blue (MB) adsorption capacities were found to increase with increasing solution pH until equilibrium point with pH values of 8. The pH of a medium is a master variable that determines the surface charge of an adsorbent through protonation and de-protonation (Kheddo et al., 2020). At acidic pH of 2, MB adsorption was found to be lower which could be attributed to the protonation of anionic groups on ceramsite resulted in de-protonation of the acid sites on ceramsite and the surface becoming negatively charged with high attractive properties. This led to increased surface diffusion of the dye molecules due to high electrostatic interactions between MB dye and ceramsite. Lower adsorption of MB at acidic pH might be due to the presence of excess H+ ions competing with

MB cations for the available adsorption sites which reduce the adsorbed amount. Since MB is a cationic dye it removed from the solution on basic medium as shown by previous reports.

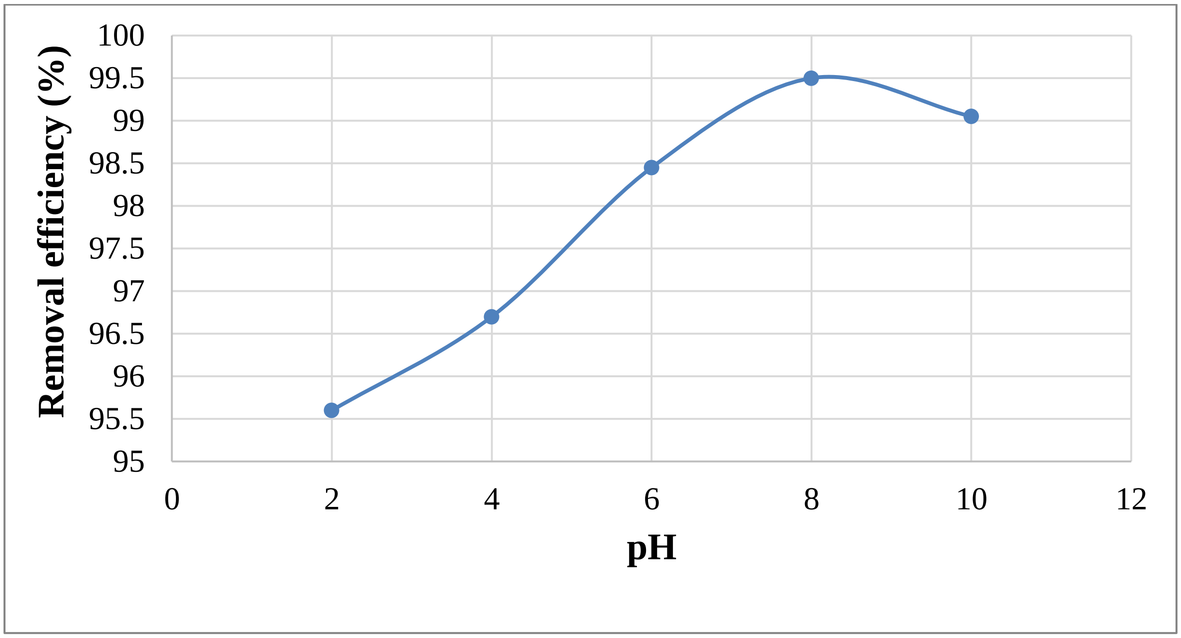


Figure 4.5: Effect of pH on MB dyeremoval by ceramsite methylene blue = 50 mg/L, adsorbent dose = 0.2/50mL and time = 60 min.

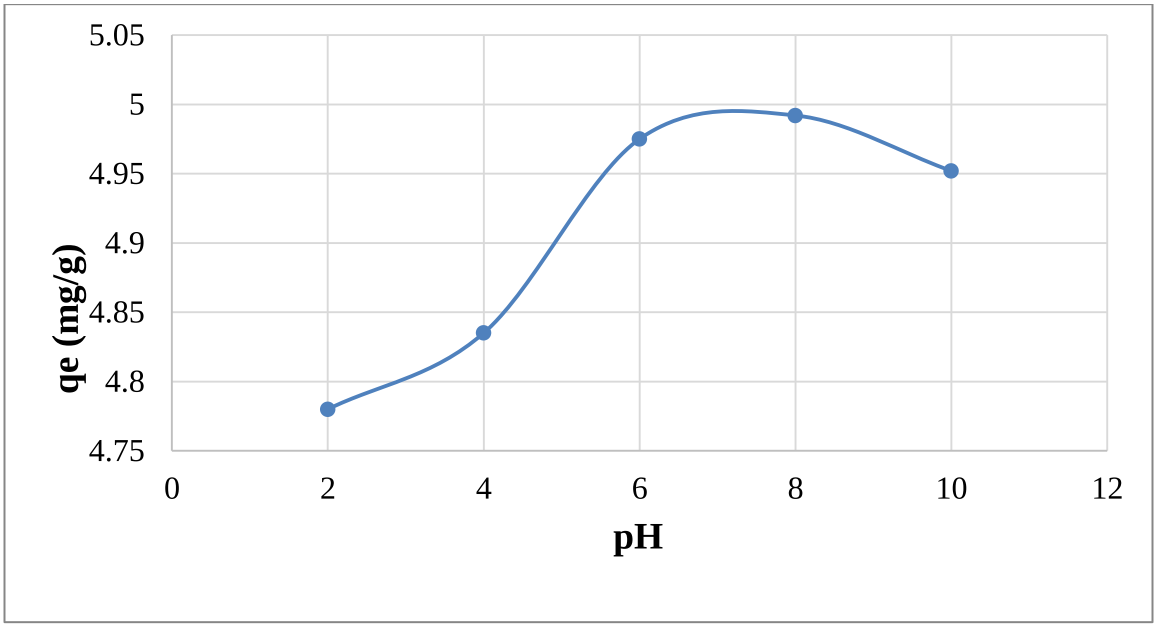


Figure 4.6: Effect of pH on MB dye uptake by ceramsite at adsorbent dose = 0.2/50mL and time = 60 min.

4.2.3 Effect of Adsorbent Dose.

The effect of adsorbent dose on MB dye removal was studied by varying adsorbent dose from 0.1 to 0.5 g and it was seen that removal efficiency increases with increasing adsorbent dose. The change in adsorbent dose from 0.1 g to 0.5 g can increase removal from 98.6 % to 99.76% for MB dye removal by keeping other factors at the center. This trend was due to increase in surface area and adsorption sites available for adsorption. As shown in figure 4.8, the adsorption capacity of adsorbents was found to decrease with increasing adsorbent dosage as the number of adsorption sites per unit mass decreases.

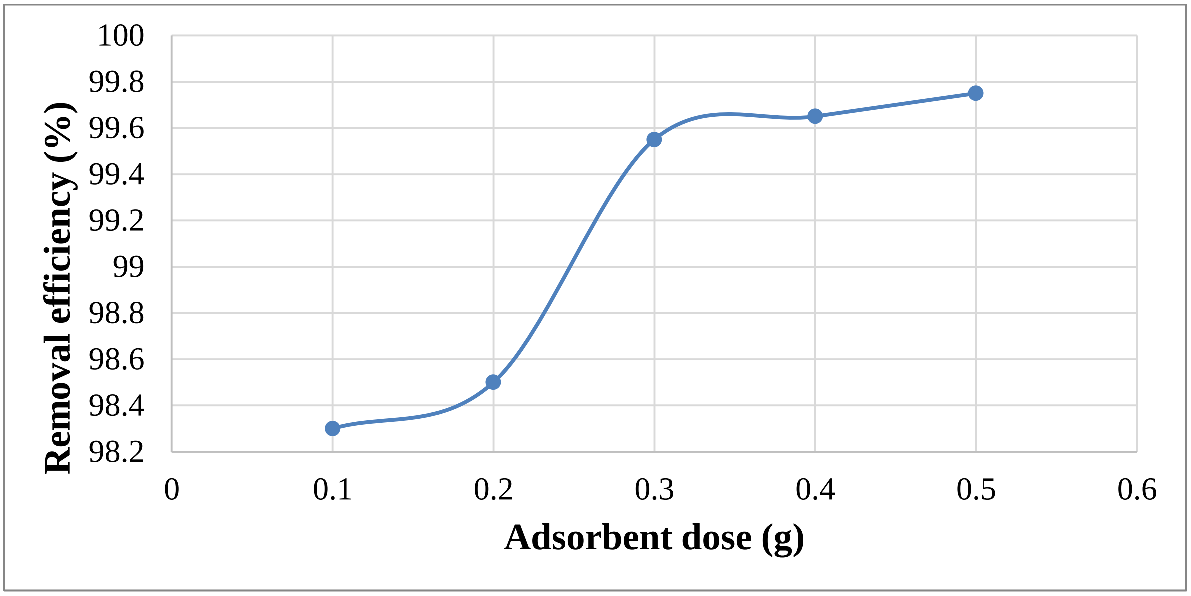


Figure 4.7: Effect of adsorbent dose on MB dye removal efficiency by ceramsite at pH = 8 and time = 60 min and MB dye concentration = 50 mg/L.

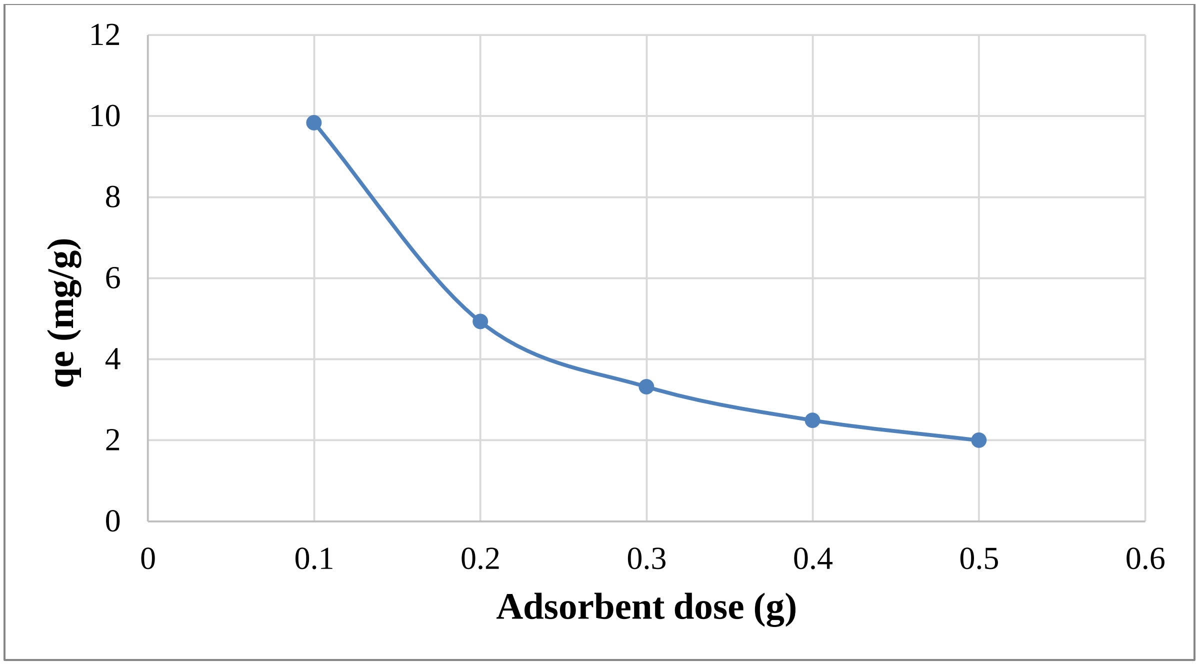


Figure 4.8: Effect of adsorbent dose on MB dye uptake by ceramsite at pH = 8 and time = 60 min and MB dye concentration = 50 mg/L.

4.2.4 Effect of Contact Time

As shown in Fig. 4.9 and 4.10, the adsorption capacity of adsorbents and percent removal of MB onto the ceramsite were found to increase drastically during the initial adsorption stage and then continue to increase at a relatively slow speed with time until a state of equilibrium was attained. The equilibrium/optimum time was found to be 90 min with removal efficiency of 99.26 min. This phenomenon is attributed to the fact that a large number of vacant surface sites are available for adsorption at the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive force between the solute molecules on the solid and bulk phase (Nasr et al., 2017).

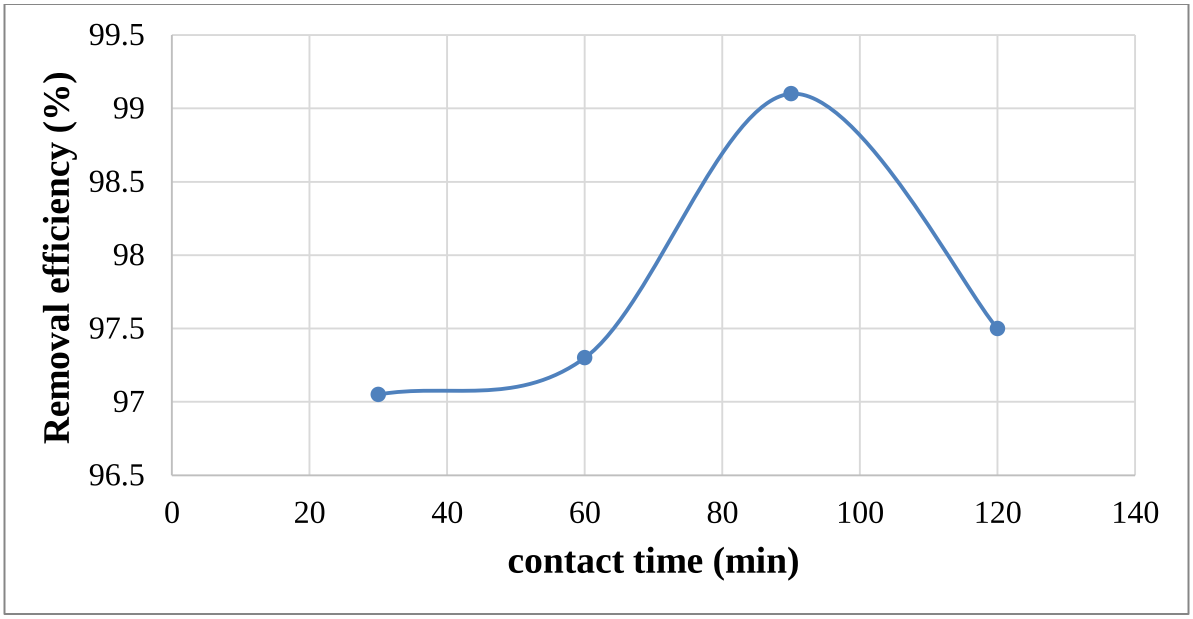


Figure 4.9: Effect of contact time on MB dye removal efficiency by ceramsite at pH = 8, adsorbent dose = 0.5 g/50mL and MB dye concentration = 50 mg/L.

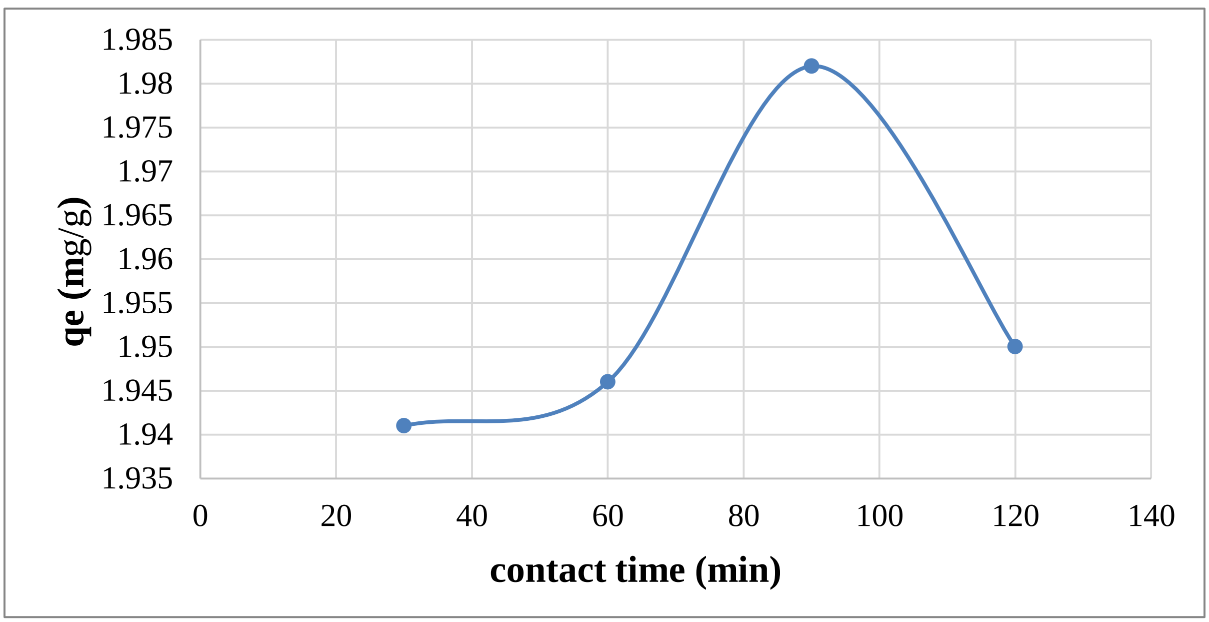


Figure 4.10: Effect of contact time on MB dye uptake by ceramsite at pH = 8, adsorbent dose = 0.5 g/50mL and chromium concentration = 50 mg/L.

4.2.2 Effect of Initial Concentration

As shown in Fig. 4.12, the adsorption capacities of ceramsite were found to increase with increase in the initial concentration of dye. however, the percent removal of MB decreases beyond 10 mg/L of dye concentration (Fig. 4.11) suggesting that the larger ratio of active adsorption sites is available at lower initial concentration that led to the observed greater percentage removal of dye at lower initial concentration but smaller at higher initial concentration (Hsini et al., 2021). Because with in increasing dye concentration immediately dye adsorbed onto the active site of adsorbent and which prevents further adsorption by repulsion force of dye on the adsorbent phase and on the bulk phase.

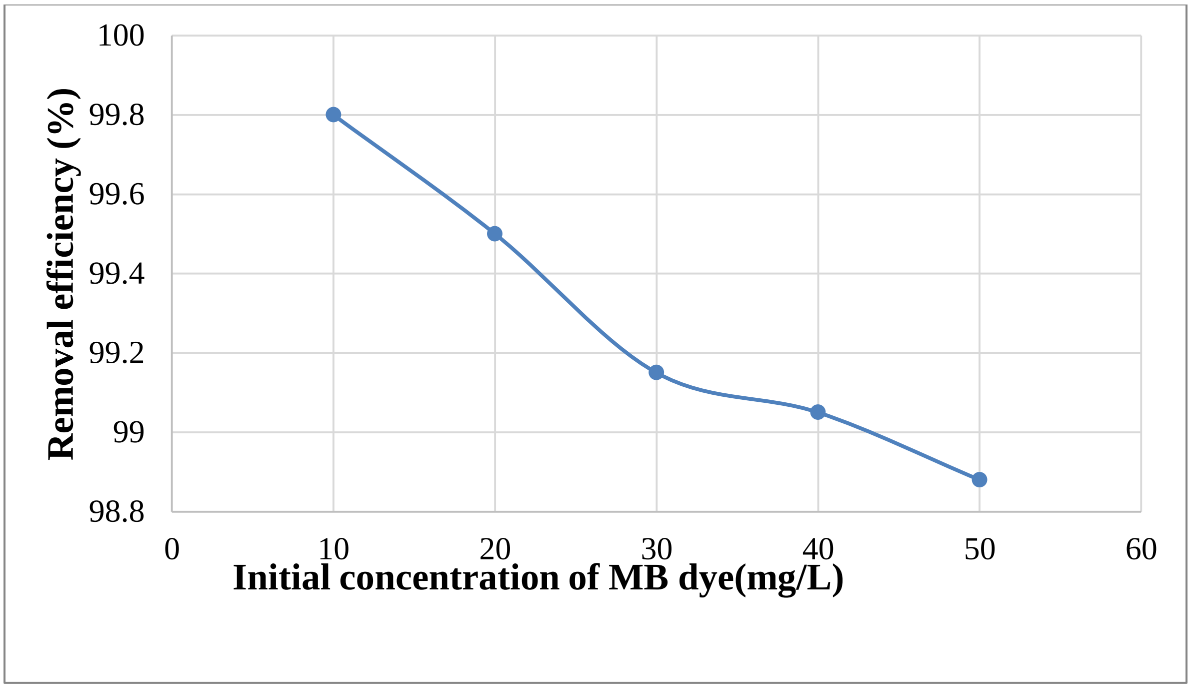


Figure 4.11: Effect of initial concentration on MB dye removal by ceramsite at pH = 8, adsorbent dose = 0.5g/50mL and time = 90 min.

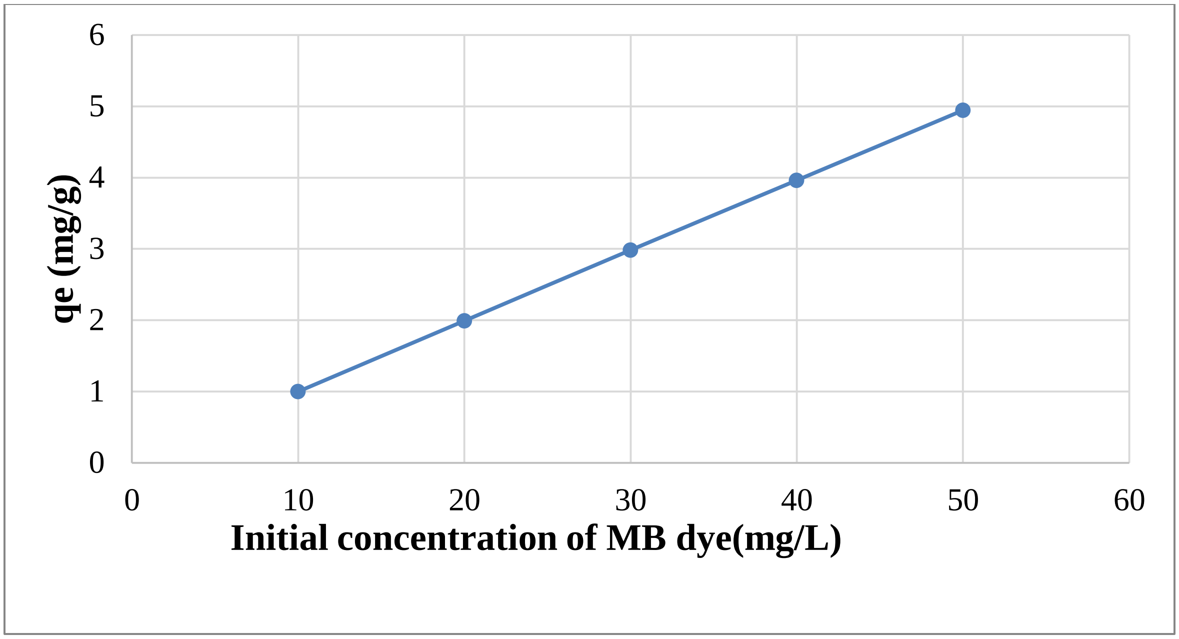


Figure 4.12: Effect of initial concentration on MB dye uptake by ceramsite at pH = 8, adsorbent dose = 0.5 g/50mL and time = 90 min.

4.3. Adsorption isotherm

In order to evaluate the behavior of molecules of MB with the adsorbent surface, the adsorption isotherms were used to analyze the experimental data. The isotherm provides a relationship between the concentration of dye in solution and the amount of dye adsorbed on the solid phase when both phases are in equilibrium. The most widely used isotherm equations are Langmuir and Freundlich equations(Yunusa & Ibrahim, 2019).

4 .3.1 Langmuir Adsorption Isotherm

The Langmuir model used to describe the formation of monolayer adsorbate on the outer surface of the adsorbent. The Langmuir isotherm is often applicable to a homogeneous adsorption surface with the entire adsorption site having equal adsorbate affinity.

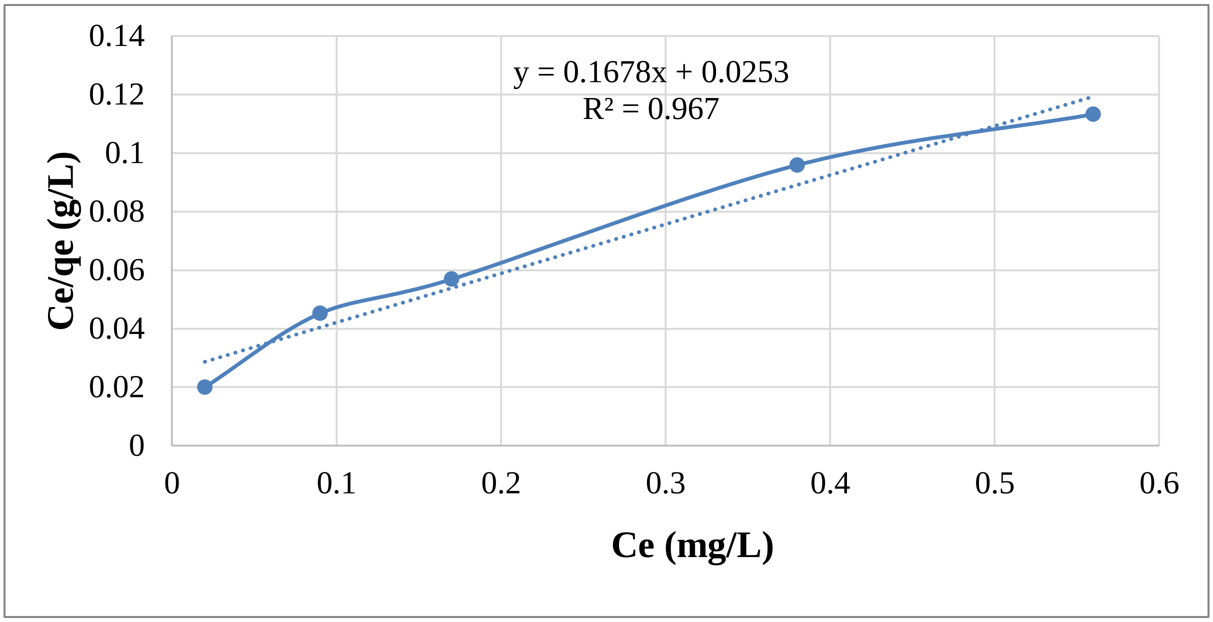


Figure 4.13: Langmuir adsorption isotherm model

Table 4.2: Langmuir adsorption isotherm parameters

Q max	39.525mg/g
KL	0.1507 L/mg
R^2	0.967
RL	0.2851
Equation	1/qe= 0.1678(1/ce) +0.0253

The RL (the separation factor) value lies between 0 and 1 which confirm that the adsorption process of MB dye is favourable on ceramsite. The value of RL is 0.2851which is indicate that adsorption of MB dye on ceramsite is favorable adsorption. R^2 is 0.967 which is less than R^2 value of Freundlich Adsorption Isotherm for this reason Langmuir adsorption isotherm parameters model does fail to describe the experimental finding.

4 .3.2 Freundlich Adsorption Isotherm

The Freundlich isotherm describe that during the adsorption process different site of the adsorbate are involved with several adsorption energy is an empirical relation for adsorption over heterogeneous surfaces.

To determine whether Freundlich adsorption isotherm model fit to the experimental value or not the graph of log qe as a y-axis and log Ce as x-axis was plotted. From linear equation the value of Kf (adsorption capacity) and 1/n was calculated and the Freundlich adsorption isotherm equation was developed.

The smaller 1/n becomes, the greater the expected heterogeneity and if n is between one and ten or 1/n was less than one, it indicates a favorable sorption process (Thiebault, 2020). As the data in Table 4.3, shows the value of 1/n is 0.4774 while n is 2.0946 confirm that the sorption of MB dye on ceramsite is favorable and R^2 is 0.9957 indicate that the sorption data is fitted well to Freundlich adsorption isotherm model.

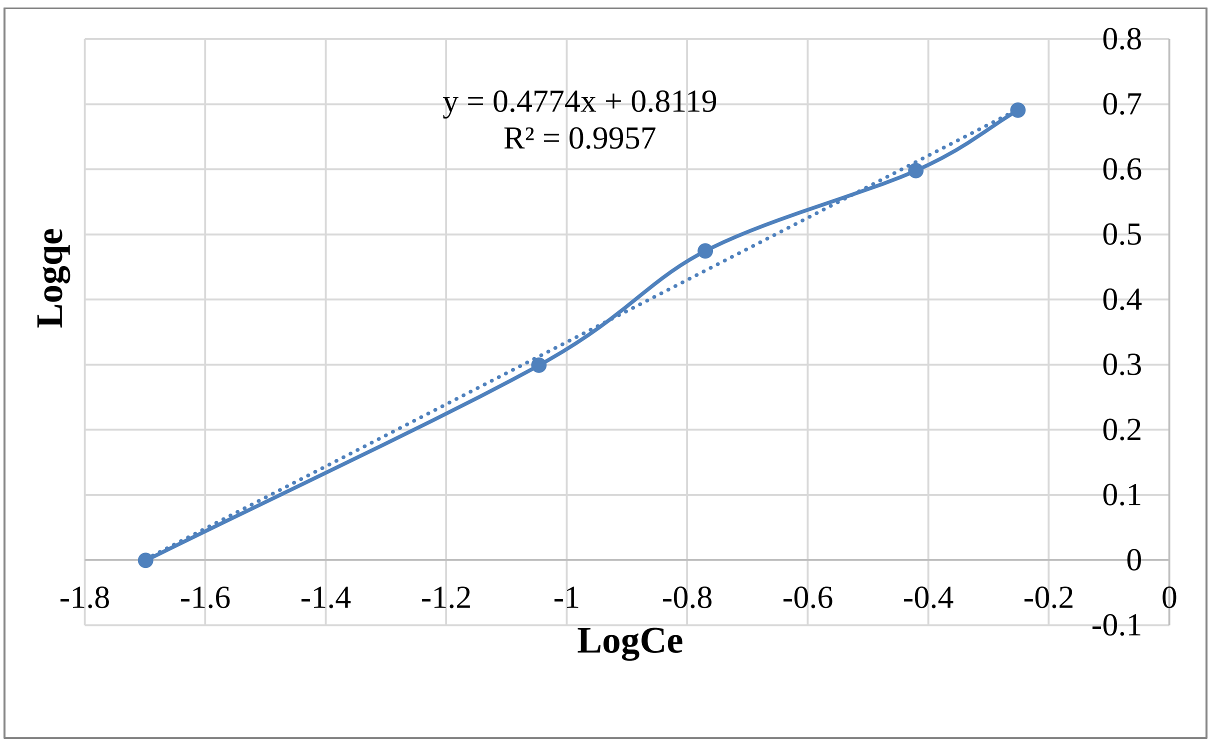


Figure 4.14: Freundlich Adsorption Isotherm

Table 4.4: Freundlich Adsorption Isotherm parameters

n	2.0946mg/g
1/n	0.4774
R^2	0.9957
Kf	6.4848
Equation	Logqe= 0.4774LogCe +0.8119

4.6 Adsorption Kinetics

Kinetics model have been exploited to test the experimental data and to find the mechanism of adsorption and its potential rate-controlling step that include mass transport and chemical reaction.in order to further understand the characteristics of the adsorption process, the pseudo first and second order kinetics order kinetic models were applied to fit experimental data obtained from batch experiments.

4.6.1 Pseudo First Order Kinetics Model

To determine whether adsorption mechanism is determined by pseudo first order or not the graph of log (qe-qt) vs. t was plotted as stated in Equation (2.10) and its linearity was observed by considering correlation coefficient value. The values of k1 and qe were calculated from slope and intercept of the plot of log (qe-qt) Vs t respectively and Table 4.5 summarize the value of the kinetics parameters. The pseudo first order plots of MB dye adsorption on ceramsite for two different concentrations (10 and 30 mg/L) are shown in Figure 4.15. The value of R^2 for the pseudo first- order was low as compared to R^2 value of pseudo- second order. The lower R^2 value obtained indicate that adsorption of MB dye on ceramsite does not follow pseudo first order kinetics.

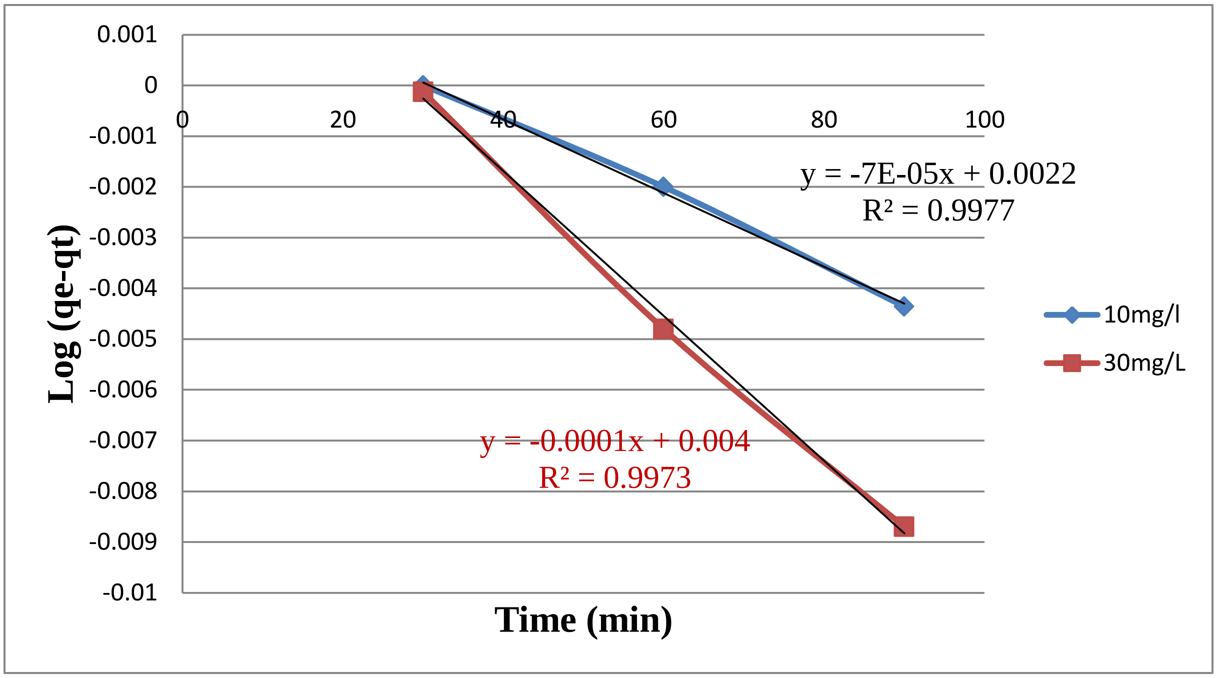


Figure 4.15: Pseudo first order kinetic curve

Table 4.5: Pseudo first order adsorption Kinetics parameters

Contanant	Concentration (mg/L)	Qe exp (mg/L)	Qe cal (mg/L)	K1	R^2
MB dye	10 mg/L	1.991	1.0050	0.40993	0.9977
	30mg/l	3.962	1.0092	0.00023	0.9973

4.6.2 Pseudo Second Order Kinetics Model

To determine whether adsorption mechanism is determined by pseudo second order or not the graph of t/qt vs. t was plotted using Equation (2.11) and its linearity was observed by considering correlation coefficient value. The values of qe and K_2 were calculated from slope and intercept of the plot of t/qt vs. t respectively and Table 4.6 summarize the value of the kinetics parameters. The pseudo second order plots of MB dye on ceramsite for two different concentrations (10 and 30 mg/L) are shown in Figure 4.16. The value of R^2 for the pseudo second- order was higher as compared to R^2 value of pseudo first order. Therefore, pseudo second- order adsorption model is more favourable to describe the adsorption kinetics of MB dye on ceramsite prepared from sewage sludge, bagasse ash and bentonite which indicate that chemisorption is the rate limiting step.

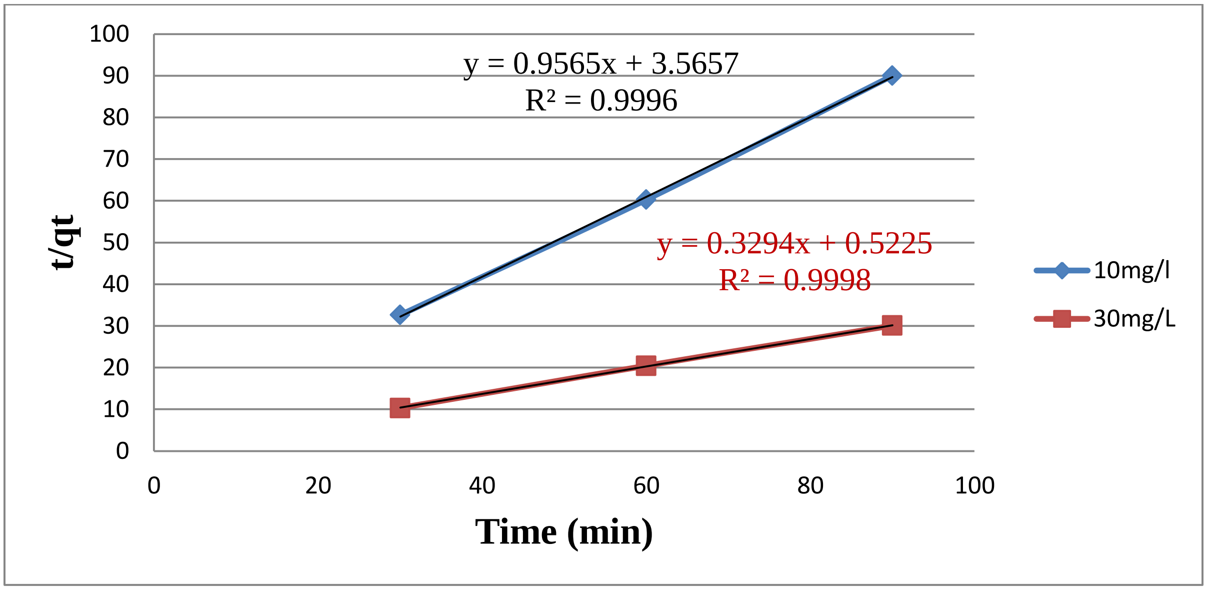


Figure 4.16: Pseudo second order kinetics curve

Table 4.6: Pseudo second order adsorption Kinetics parameters

Contaminant	Concentration (mg/L)	Qe exp (mg/L)	Qe cal (mg/L)	K2	R^2
MB dye	10 mg/L	1.991	1.0454	0.2566	0.9996
	30mg/l	3.962	3.0358	0.2076	0.9998

4.7. Reusability Experiment

The regeneration and reusability of adsorbent is one of the important aspects to be considered for applicability of the adsorbent in aqueous solution. From the economical point of view, regeneration and reusability of the adsorbent is cost saving method. Also it helps to avoid the problem of adsorbent disposal which may lead to secondary (Santhi et al., 2009). From figure

4.17, the efficiency of the adsorbent for the removal of MB dye dropped to 94.6% after 3 consecutive usages. Overall, it can be concluded that, ceramsite has good regeneration and reusability potentiality.

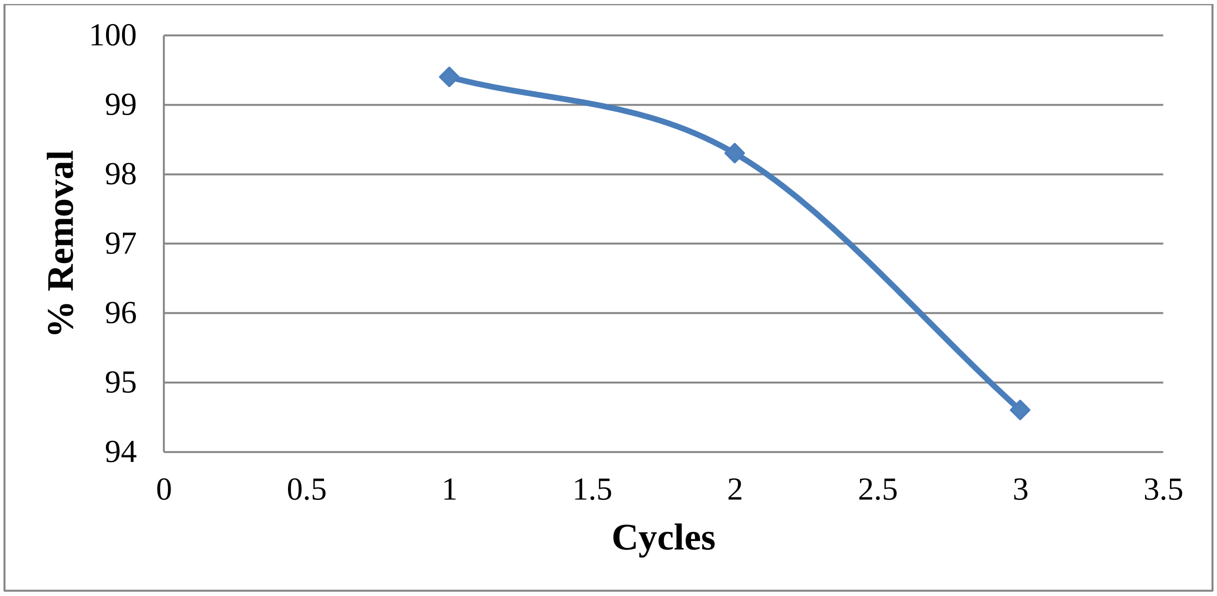


Figure 4.17. Regeneration and reusability of ceramsite for the adsorption of MB dye.

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

The viability and prospects of future existence of a manufacturing industry such as textile industries depend on the development or use of locally available raw materials and wasted resources to substitute imported raw materials demand in their unit operations including in the wastewater treatment plant. That would also promote appropriate utilization of the waste instead of discarding it to the environment, which causes adverse effects on human beings and environments. To this end, this study investigates the possibility of developing ceramsite from locally available raw materials bentonite and by using waste materials dewatered sewage sludge and sugarcane bagasse fly ash to for its application to remove methyl blue from aqueous solution.

The different analysis result of the ceramsite confirmed that:

- Ceramsite prepared from dewatered sewage sludge, bagasse fly ash, and bentonite at the optimized mixing ratio of (4:3:4), respectively, at the optimized preheating temperature of 250^{o}C for 20min, and at the optimized calcination temperature of 600^{o}C for 30 minute contained Quartz and calcite as the major crystalline phase and the illite, Kaolinite and montmorillonite clay minerals as the minor phase. The high quartz and calcite content promotes the formation of the highly porous and less dense ceramsite which significantly influence its adsorption efficiency.

- The ceramsite has maximum removal capacity of 9.88 mg/g with removal efficiency 99.8% at optimized contact time of 90 minutes, initial MB dye concentration of 10 mg/L and 0.5g of ceramsite dose at room temperature with stirring rate of 150 rpm. In which its efficiency dropped to 94.6% after 3 consecutive usages. Indicated the prepared ceramsite has excellent material for removal of MB with good regeneration and reusability potential.

- Adsorption process is well described by Freundlich model with high R^2 value of 0.9996 which indicates the adsorption mechanism is mainly of chemisorption; and the data from kinetic experiments was found to fit well with pseudo-second order kinetic model.

- In general, ceramsite prepared from sewage sludge, bagasse ash and bentonite can be used as low cost, and environmentally friendly adsorbent for the removal of MB dye from aqueous solution.

5.2. Recommendation

From the result of the study the following recommendation has been forwarded. As a byproduct of wastewater treatment plant, sewage sludge and as a byproduct of sugar manufacturing industry, bagasse ash is low cost, environmentally friendly and easily available resource to be used as an adsorbent for MB dye removal from wastewater and it should not be simply discarded to the environment.

ceramsite prepared from sewage sludge, bagasse ash and bentonite had been shown to have the potential in MB dye from aqueous solution. To investigate effectiveness of ceramsite further the following studies could be recommending to other researchers.

- ✓ It is better to perform the BET in order to investigate the surface area.
- ✓ The efficiency of this material should also be investigated for the removal of heavy metals, BOD and COD from aqueous solution and also the application of the material on real wastewater containing all sorts of pollutants.
- ✓ Characterization of the ceramsite using advanced techniques such as XRF; to determine the chemical composition of the adsorbent (ceramsite).

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APPENDICES

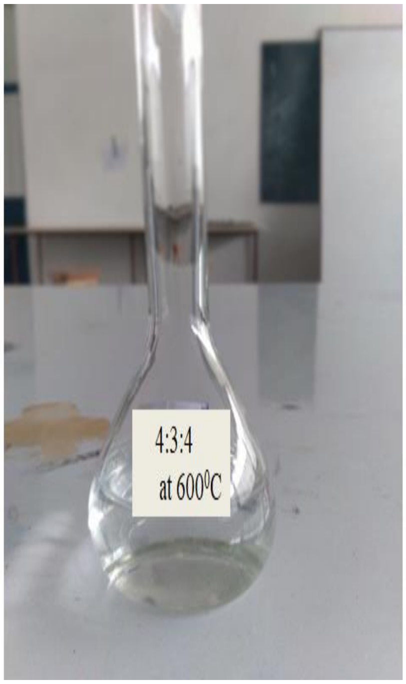
Pre-test for selection of the best ceramsite

- Pre-test for selection the best ceramsite prepared from dewatered sewage sludge (DSS), bagasse fly ash, and bentonite by different sintering temperature (600^{o}C, 700^{o}C and 900^{o}C) and varying mixing ratio of materials (dewatered sewage sludge (DSS), bagasse fly ash, and bentonite (4:3:4, 5:2:4 and 6:1:4), respectively.
- The Pre-test result is shown below:

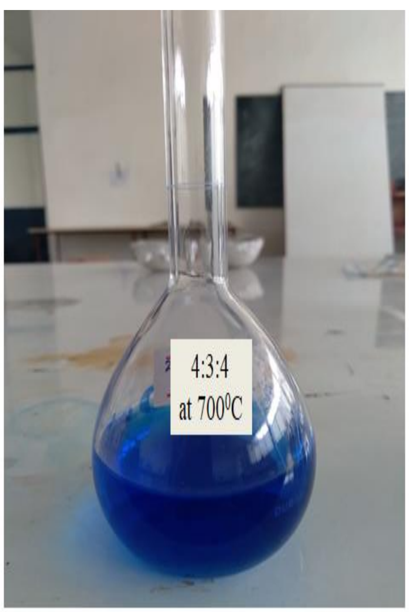
- Ceramsite prepared at 600^{o}C by different three formulation (dewatered sewage sludge (DSS), bagasse fly ash, and bentonite by ratio of (4:3:4, 5:2:4 and 6:1:4)) respectively are effective raw material (Ceramsite) for removal of methylene blue dye.

- The percentage removal of dye (methylene blue) at 600^{o}C by mixing dewatered sewage sludge (DSS), bagasse fly ash, and bentonite by ratio of (4:3:4) respectively is 99.68%.

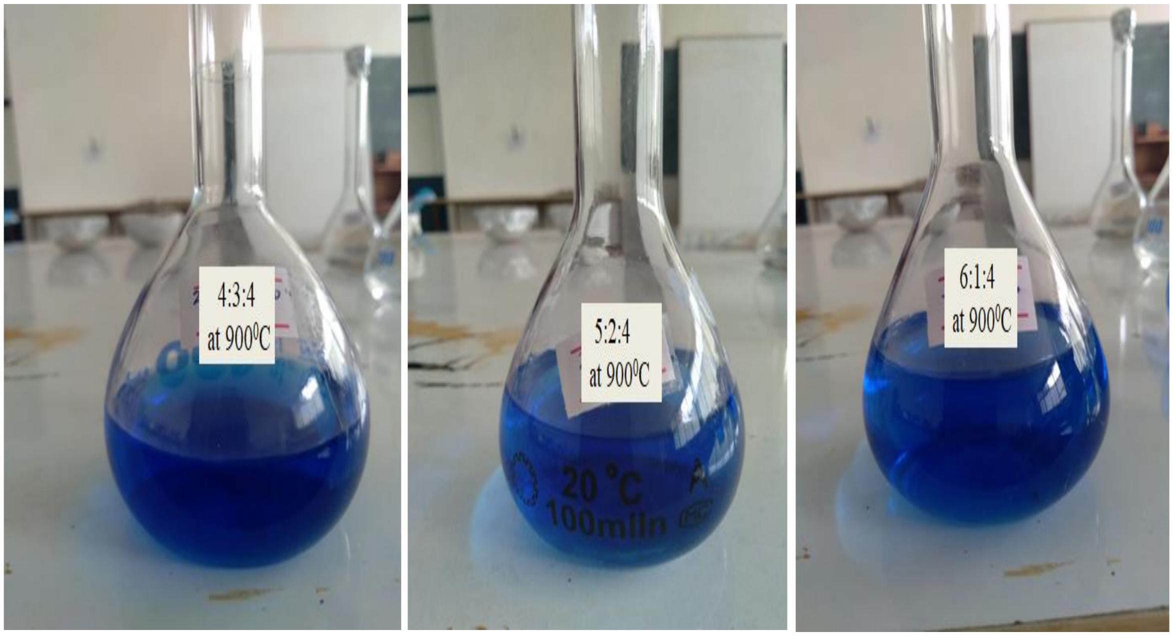
- The percentage removal of dye (methylene blue) at 600^{o}C by mixing dewatered sewage sludge (DSS), bagasse fly ash, and bentonite by ratio of (5:2:4) respectively is 99.15%.
- The percentage removal of dye (methylene blue) at 600^{o}C by mixing dewatered sewage sludge (DSS), bagasse fly ash, and bentonite by ratio of (6:1:4) respectively is 99.1%.



- ceramsite prepared at 700^{o}C by different three formulation (dewatered sewage sludge (DSS), bagasse fly ash, and bentonite by ratio of (4:3:4, 5:2:4 and 6:1:4)) respectively are less adsorbed methylene blue dye on the site surface area (less effective adsorbent when we compare ceramsite prepared at 600^{o}C for removal of methylene blue dye).



- ceramsite prepared at 900^{o}C by different three formulation (dewatered sewage sludge (DSS), bagasse fly ash, and bentonite by ratio of (4:3:4, 5:2:4 and 6:1:4)) respectively are less adsorbed methylene blue on the site surface area (less effective adsorbent when we compare ceramsite prepared at 600^{o}C for removal of methylene blue dye).



So, based on pre-test results the best material (ceramsite) used for removal of methylene blue is ceramsite prepared at 500^{o}C by mixing dewatered sewage sludge (DSS), bagasse fly ash, and bentonite by ratio of 20:15:20 respectively.

preparation of ceramsite:

Figure. 7.1. Raw materials used for preparation of ceramsite.

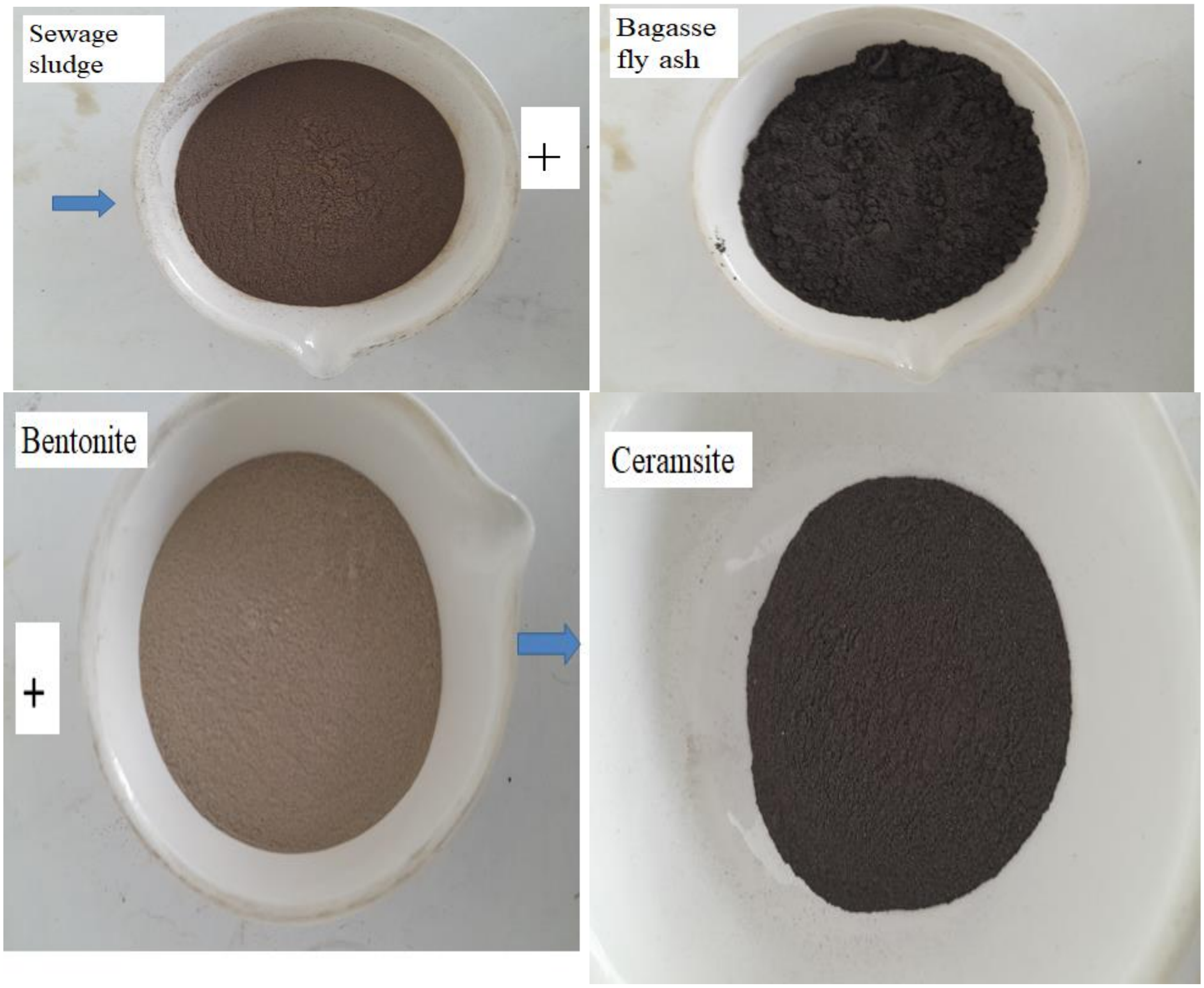


Figure. 7.2: preparation of ceramsite.

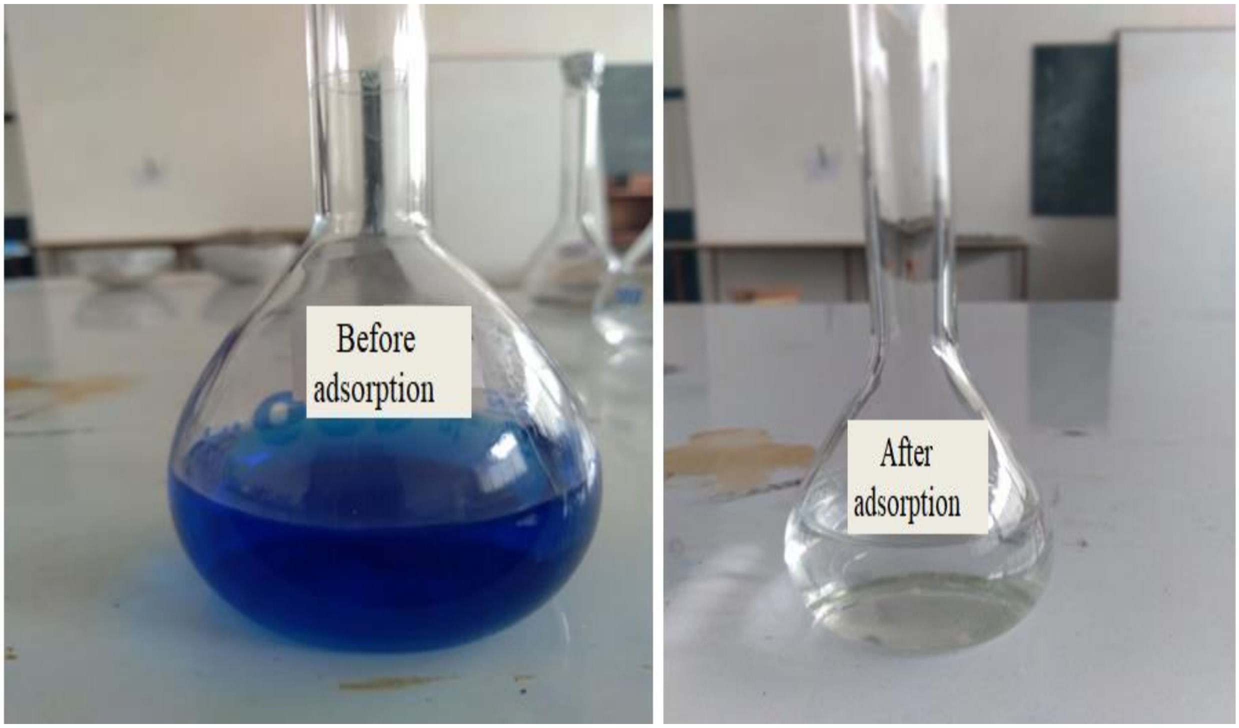


Figure. 7.3: Dye solution before and after adsorption process with MB dye.