Extraction of Silica from Sorghum Stalk and Application for Adsorption of Methylene Blue from Aqueous Solution

Gezahegn Mebiratu, Amare Ayalew and Hirpo Hinsene

[1]Debre Berhan University, Department of Chemistry, P.O.Box 445, Debre Berhan, Ethiopia

[2]The Federal Democratic Republic of Ethiopia Chemical and Construction Inputs Industry Development Institute, P.O.Box 4124, Addis Ababa, Ethiopia

*Corresponding author. E-mail: aayalew2@gmail.com

Abstract

In the world, different pollutants from industries released every day to the environment without treatment. For this studies synthesized silica from Sorghum Stalk was used for adsorption of Methylene Blue dye from aqueous solution. Agricultural wastes used for the preparation of adsorbents, among those sorghum stalk is the one which was used in this study. The main raw material for synthesis of silica sorghum stalk is easily available in Ethiopia. Synthesized silica was characterized by modern spectroscopic technique like x-ray powder diffraction (XRD), Fourier transform infrared spectrometry (FTIR), Uv-visible spectrophometry (UV-Vis) and inductively coupled plasma-optical emission (ICP-OES). From ICP-OES the highest silica (SiO_2) with value (8,265.21 mg/kg) was obtained. The influence of operating parameters like pH, dosage, contact time and concentration, on the removal of MB were investigated. Depending on the above parameters, SiO_2 was able to remove rapidly at pH (10), dosage (0.4g), time (180 min) and concentration (5ppm) of Methylene blue. By this adsorbent around 96.5 % removal efficiency of methylene blue dye was achieved. The studies adsorption isotherm fit with Freundlich isotherm with R^2 of 0.99 and adsorption kinetics of Pseudo-first-order adsorption Kinetics (R^2= 0.995).

Keywords: Adsorbent, Isotherm, Methylene blue, Silica, Sorghum stalk

1. INTRODUCTION

Crops are naturally produced under adverse conditions. Crops are well adapted to a wide range of rainfall as well as temperature. Numerous crops are cultivated in different parts of Ethiopia. Among those crops sorghum is the one which cultivated in Ethiopia. Sorghum is one of the major essential crops grown in the poorest and most food insecure regions of Ethiopia. Ethiopian is often regarded as the center of domestication of sorghum because of the greatest genetic diversity in the country for both cultivated and wild forms (Fetene *et al*., 2011).

Ethiopia is the second country in the production of sorghum in Eastern and Southern Africa country next to Sudan. Sorghum production has significantly increase year to year, for example the production of sorghum in 2004/05 was 1.7 million tones but in 2010/11 it increases approximately 4.0 million tones. Sorghum is the second most important cereal produced in Ethiopia. The large enhancement in sorghum production is driven by both land expansion and yield improvement (Di Marcantonio and Demeke, 2013).

Silica is a chemically inert, non-toxic material composed of amorphous silicon dioxide. It has an internal network of interconnecting microscopic pores, yielding a typical surface area of (700-800 m^2/g). Silica was patented in 1919 for use in the adsorption of vapors and gases in gas mask canisters during the time of World War I. During World War II, it was commonly used as a dehydrating agent to protect military and pharmaceutical supplies, among a number of other applications. Silica are a stiff three-dimensional linkage of colloidal silica. Amorphous mesoporous silica are categorizedbased on the synthesis process as an aqua gel, xerogel and aerogel. Amorphous mesoporous silica has been effectively extracted from several agricultural bio-resources such as sugar-cane, rice husk ash, corn cob ash, bagasse ash, coffee husk ash and wheat huskash. Techniques such as sol–gel, gasification and acidleaching have been investigated to produce pure amorphous silica echniques such as sol–gel, gasification and acidleaching have been investigated to produce pure amorphous silica (Patrick et al., 2019).

Methylene blue, a heterocyclic basic dye that contains three water molecules in hydrated form ($C_{16}H_{18}N_3SCl.\ 3H_2O$). Methylene blue is commonly employed for dying cotton, paper, silk, wood, and wool. Methylene blue dissociates into Methylene blue cation and chloride in aqueous solutions. Methylene blue is not strongly hazardous but give rise to adverse effects on human

health, including increased heart rate, respiratory sensitization, nausea, allergic dermatitis, dizziness, vomiting, and irritation of the gastrointestinal tract. Methylene blue causes convulsion, cyanosis, sweating, confusion, and short periods of difficult breathing on in halation. Its degradation products in the body, such as toluidine, benzidine, and other aromatic components, may cause cancer and mutations.

Methylene blue has several advantages such as the price is relatively cheap, easy to obtain, good solubility, and is a basic dye. In the coloring process, methylene blue is bonded about 5% while the remaining 95% is wasted as waste, so the methylene blue waste in the aquatic environment is very large (Gong *et al*., 2015. Methylene blue waste in addition to damaging aquatic ecosystems it also disrupt human health (Gürses*et al*., 2014). Direct ejection of dyes containing wastes into the environment cause the formation of toxic carcinogenic breakdown products. The highest rates of toxicity were found amongst basic and diazo direct dyes so it is highly needed to reduce dye concentration in the wastewater Waste water from textiles, cosmetics, printing, dying, food processing, and paper-making industries is polluted by dyes. (Wang *et al*., 2008).

Almost all dyes are poorly biodegradable or resistant to environmental conditions. Dyes cause major problems in the treatment of wastewater from the dyeing industry. Thus, it is essential to have effective treatments for the removal of dyes before discharging them into the environment (Munagapati et al. 2018). In recent years, numerous methods are being used for the treatment of dye-contaminated effluents such as oxidation (Vincenzo Naddeo 2013), ion exchange (Skipton and Dvorak 2014), adsorption (Ayub and Khorasgani, 2014, Neway and Hirpo, 2020), photodegradation (Iovino et al. 2017), anodic oxidation (Godini et al. 2013, and biological treatment (Alvarino et al. 2018). However, adsorption was proven as one of the best methods for the removal of various dyes present in the water system (Bouaziz et al. 2015, Dominic et al., 2019, Neway and Hirpo, 2021) considering its convenience, ease of operation, simple designs, and cost efficiency. For this study Silica prepared from Sorghum Stalk was synthesized and applied for removal of Methylene blue dye from aqueous solution.

2. MATERIAL AND METHODS

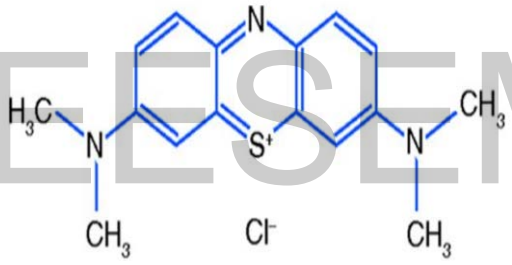
2.1 Description of Study Area and Experimental Site

2.1.1 Experimental site

Syntheses of silica from Sorghum, UV-Vis spectrophotometry for determination of methylene blue from wastewater were conducted at the Debre Berhan University, Chemistry Research Laboratory. The Inductively coupled plasma optical emission spectrophotometers (ICP-OES) at Horticoop Ethiopia (Horticulture) PLC, Debere Zeit, XRD characterization of adsorbent was determined at the Chemistry Department of Adama Science and Technology University (ASTU) and FTIR characterization was done at Cadila pharmaceuticals PLC, Gelan, Ethiopia.

2.2. Chemicals

All chemicals and reagents used in the study were of analytical grade and used without further purification. Methylene blue ($C_{16}H_{18}N_3ClS$) obtained from Fine Chemicals Company was used to prepare standard solutions of the adsorption Study. HCl and NaOH used to adjust pH and a buffer solution (pH 4, 7 and 10) were used to calibrate the pH-meter.



Structure of methylene blue dye

2.3. Apparatus and Instruments

The most common laboratory apparatus which were used during the experiment of study included different sized beakers, Erlenmeyer flasks, funnels, graduated cylinders, volumetric flasks, and test tubes, droppers, glass pipettes, spatula, measuring cylinders, stirrer, analytical balance, conical flasks, cotton wool and a 60 cm × 8 mm glass column. All glassware (conical flasks, measuring cylinders, beakers, pipettes etc.) were manufactured by Borosil / Rankem were used throughout the experiment and there were washed by distilled water and 2% nitric acid before used for any purpose. Whatman No. 42, Sieve, knife, An electronic beam balance, Pistil and mortar, drying oven, Muffle Furnace, pH meter and shaker.

Instruments used were XRD recorded by PANalytical X'pert pro diffractometer at 0.02 degree/sec scan rate using Cu-kα1 radiation (1.5406 A^0, 45 kV, 40 mA) and used to determine

sizes of the primary crystallite (Ds) of adsorbent from the XRD. FTIR analysis was also carried to know what bonds are present in the prepared silica in the range of 4000-400 cm^{-1} wave number. Uv-Vis and ICP-OES were used for this study.

2.4. Methylene Blue Sample Preparation

A stock solution (1000 mg/L) of methylene blue was prepared by dissolving appropriate amount of 1 g MB in 1 L of deionized water. The intermediate (10, 20, 30, 40 and 50 mg/L for MB) were prepared by suitable dilution of the stock solution.

2. 5. Sampling and sample preparation

The adsorbent (Sorghum stalk) sample was collected from Debre Berhan, Ethiopia in randomly sampling technique from the farm land and the collected samples were mixed to prepare adsorbent composite sample. Adsorbent is the material upon whose surface the adsorption takes place is called an adsorbent. For this study sorghum stalk was used as an adsorbent because it is a low cost bio sorbent, easily available and non -toxic.

Figure 1. Sorghum Stalk

The collected sorghum stalks was washed with distilled water for several times to remove all the dirt particles which are present in sorghum stalk in order to minimize or avoid contamination during the time of the preparation of silica gel. The sample which was washed by using water was dried by direct sunlight. The washed sorghum stalk was cut into small pieces until its size becomes (1-3 cm) as well as it was powdered using pistil and mortar. The dried samples were heated in a muffle furnace for 3 hrs at 600 °C. Then ground and finally screened to obtain a particle size range of 1 mm size sieve and then stored in plastic bottles for further use.

Figure 2. How to prepare silica from sorghum stalks.

2. 6. Preparation of Silica

The extraction of silica was adapted from the method which was reported in the literature (Gnanounou*et al*., 2005) with in minor changes. In this study silica was synthesized by following the procedure which mention below. 4 g of sorghum ash was mixed with 40 ml of 60% HCl solution and then the solution was heated and stirred for 30 minutes to avoid the heavy metal which present in the silica and the solution was stayed for 3 hr. Then the solution was filtered and the solid part of the solution was taken.

The solid part of the sample was washed using distilled water until the pH becomes from 6.5 up to 7 further removing of the heavy metal and sample solution was decanted. After decantation the sample was placed in oven for 2 hrs. Then the solid part was taken from the oven and it placed in clean place till it cooled and measured. The dried sample was placed in clean and dry place. 3 g of the sample was obtained and it was dissolved in 30 ml of 4 M NaOH and it refluxed

for 8 hrs. Then the refluxed sample was placed for 30 minutes until it becomes cool and the solution sample was filtered and the liquid part was taken and it was washed by using distilled water until its pH becomes 6.5 up to 7.

Finally the liquid sample was titrated by using concentrated HCl simultaneously stirring and the silica gel was obtained. Then the gel placed in clean and dry place for 24 hrs. The liquid part of the solution was decanted and then it placed in an oven for 24 hrs. The obtained Silica was used for adsorption study of methylene blue studies.

2.7. Characterization

2. 7. 1. X-ray Diffraction

The powder XRD patterns were recorded by PANalytical X'pert pro diffractometer at 0.02 degrees/s scan rate using Cu-kα 1 radiation (1.5406 Å, 45 kV, 40 mA) to investigate the crystal structure of Silica.

2. 7. 2. Fourier Transform Infra-Red (FT-IR) Spectroscopy

FTIR spectra were obtained from the pelletized of the powder sample mixed with KBr using a SHIMADZU-IR PRESTIGE-2 Spectrometer and it indicate the presence of functional group which present in the prepared silica and also it has an additional advantage to confirm the configuration of the organic molecules.

2. 7. 3. UV-Visible Spectrometers

The UV–visible absorption spectra were recorded using a Shimadzu 2450—SHIMADZU spectrometer. The UV region ranges from 190 to 400 nm and the visible region from 400 to 800 nm. Then the maximum absorption of MB determined. In these study UV-visible spectrometers was used to measure absorption or amount of MB adsorbed by adsorbent.

2. 7.4. Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP- OES)

Inductively Coupled Plasma Optical emission spectrophotometers (ICP), or plasma in short, is an ionized gas at an extremely high temperature. It is the fourth state of matter besides gas, liquid, and solid. It used to determine elements and oxide present in the prepared silica.

2.8. Batch Adsorption Phenomena of Methylene Blue

All experiments were carried out in batch mode. The batch adsorption studies were conducted at room temperature by agitating (150 rpm) weighed quantities of the adsorbent in 50 ml of methylene blue (MB) at the optimized pH, contact time and does of adsorbent. After shaking the sample was taken and filtered by Whatman membrane filter paper of pore size 0.45 µm using a

syringe. Finally, the sample was analyzed by UV-Vis spectrophotometry at 665 nm. 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.

2. 8. 1. The Effect of pH

The effect of pH on adsorption of methylene blue dyes from aqueous solution was investigated by varying the pH from the range of 2 up to 10 and then the optimized pH was selected for the adsorption of methylene blue dye from aqueous solution.

2. 8. 2. The Effect of Adsorbent Dose

The effect of adsorbent dose on the adsorption of methylene blue was studied to find out the optimum adsorbent dose and , 0.005g, 0.01g, 0.015g, 0.2g and 0.4 g were added to four vials contains 50ml of 20mg/L MB dye solution at optimized pH.

2. 8. 3. Optimizing of Contact Time

The adsorption of methylene blue on the adsorbent was studied as a function of shaking time at 20 ^{0}C. A sample of 50 ml of dye (20 mg/L) at optimized pH and dosage for 30, 60, 90, 120, 150, and 180 minutes and optimum time obtained.

2.8. 4. The Effect of Initial Concentration

To determine the optimum concentration of adsorbate 5, 10, 20, 30 and 40 mg/L concentrations of methylene blue dye (adsorbate) were prepared and analyzed at optimum pH, dosage and time.

2. 9. Adsorption Experiments

The effects of pH, dose of adsorbent, concentration of methylene blue solution and the contact time on adsorption of methylene blue dye were studied. Equilibrium isotherm studies were conducted by varying initial concentration of methylene blue dye solution and adsorbent dose . Finally the sample was analyzed at 665nm.

The proportion of dye removal (% removal) is recognized as the ratio disparity of the dye concentration before and after adsorption to the initial concentration of dye in the aqueous solution and was calculated by the following equation (Yu et al., 2020).

$$\text{Removal Efficiency (\%)} = [(C_0 - C_e)/ C_0] \times 100 \quad \ldots\ldots (2.1)$$

Where, C_0 is the initial concentration (mg/L) of methylene blue dye in the sample and Ce is the final concentration (mg/L of methylene blue dye) in the sample solution after treatment. In this

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

$$q_e = (C_o - C_e) \times V/M \quad \text{.....} \quad (2.2)$$

Where C_0 = Initial concentration of solution (mg/l), C_e = Equilibrium concentration of solution in (mg/l), V = Volume of solution in liter and M = mass of adsorbent used in g

3. RESULT AND DISCUSSION

3.1. Optimization of Synthesized Silica

Some physicochemical properties of the prepared silica samples are presented in Table 1

Table 1. The physical properties of synthesis silica

Physical properties	Observation
Physical state	Solid
Color	White and Red
Odor	Odorless
Solubility	Soluble in water

In this studies two synthesized two silica were compared. As shown from below (Figure 3) the adsorption capacity of white sorghum (WSS) was higher (97.79%) than that of red sorghum (RSS) (91.91%). So for this study the WSS was selected used for further adsorption studies.

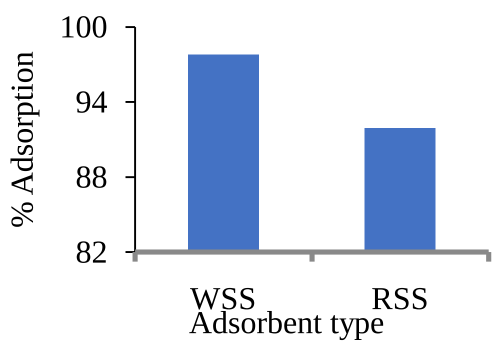


Figure 3.Compression of adsorption of capacity of white sorghum (WSS) and red sorghum (RSS)

3.2. Characterization of Silica

3. 2.1. XRD analysis

The major reflection or peaks of crystalline form of silica occur at Bragg 2θ angles of 27.2, 32.4° and 45.2° (Figure 4). It can be observed that no defined peaks corresponding to those Bragg 2θ angles are found in both the cases. A rather broad peak spanning 2θ angle was observed for silica which this result indicates that the material was amorphous and it contains pure SiO_2. In addition to this the smoothness of the band indicates that multiple washings with distilled water was efficient.

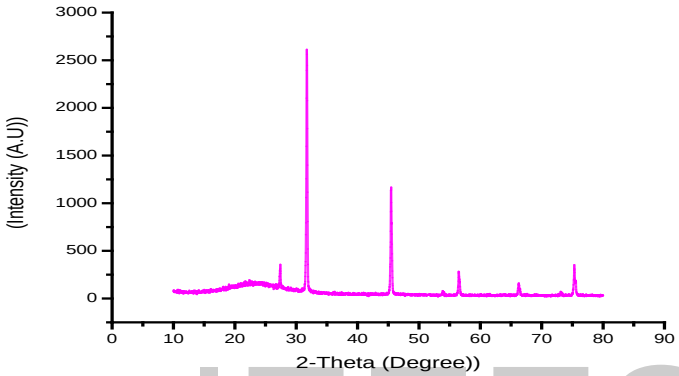


Figure 4. XRD pattern of synthesized silica.

3. 2.2. FTIR Analysis

The functional group present in the synthesized silica made from was checked using the instrument (Figure 5) before and after adsorption of MB. Before adsorption bands were observed on of silica at ~3399.84, ~1635.87,1068.14, ~953.17 and ~791.9 cm^{-1}.The broad band that observed at 3399.84 cm^{-1} is due to the stretching vibration of the O-H bond from the silanol groups (Si-OH) and physically adsorbed water. The higher value of stretching observed due to the presence of hydrogen bond. The long and sharp band at 1068.14 $cm^{-1}$is observed due to the presence of Si-O-Si asymmetric stretching vibration of oxygen atom in silicon atom on the other hand the short and sharp band at 791.9 cm^{-1} has been indicated the network Si-O-Si symmetric bond stretching vibration of oxygen atom in silicon atom or oxygen silicon starching. The band around 461cm^{-1} is associated with a network O-Si-O (SiO_4 tetrahedron) bond bending vibration modes and it used us a reference.

The following bands were observed on of silica after adsorption of methylene blue those are ~ 3217.31~ 1084.39, ~ 950.48 and ~ 798.59 cm^{-1}.The broad band that observed at~ 3217.31 is due

to the stretching vibration of the O-H bond from the silanol groups (Si-OH) and physically adsorbed water. The higher value of stretching observed due to the presence of hydrogen bond. The long and sharp band at 1084.39 cm^{-1} is observed due to the presence of Si-O-Si asymmetric stretching vibration of oxygen atom in silicon atom on the other hand the short and sharp band at 798.59cm^{-1} has been indicated the network Si-O-Si symmetric bond stretching vibration of oxygen atom in silicon atom or oxygen silicon starching.

The band that observed after adsorption is less than that of before adsorption this is because of the interaction between silica and methylene blue. The occurrence of absorption bands from the vibrations of the Si-OH bond, Si–O–Si bond, Si–O bond and O–H bond in the infrared spectrum shows that SiO_2 is present in the sample. Based on the above analysis or information, the composition of the produced materials must be SiO_2.As general bond shift shows the adsorption of MB on adsorbent.

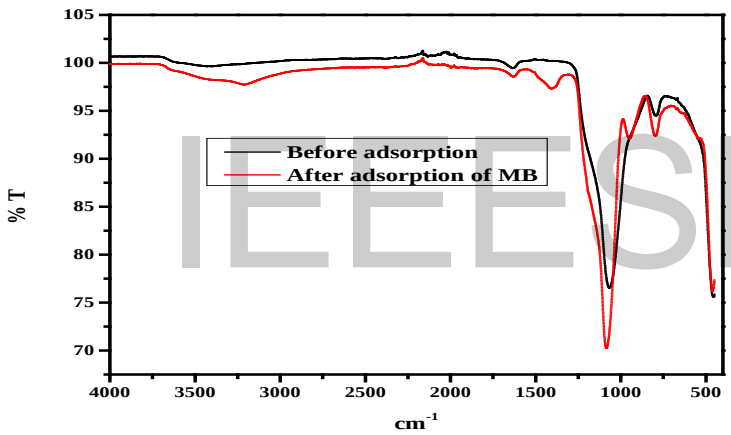


Figure 5.The spectra of FTR for silica

3.2.3. ICP-OES result

The element, ions and compounds contents of silica samples were determined using ICP-OES. The concentration or the amount of sodium was higher than the other elements/ ions/ compounds which were demined in the sample of solid silica. The concentration or the amount of copper was lower than the other elements/ ions/ compounds which were demined in the sample of solid silica. The distribution of the concentration of elements or ions or compounds in silica samples which were extracted from sorghum stalk and that collected from Debre Berhan had order of sodium > silica > phosphorous > boron > calcium > potassium >sulphate> iron > molybdenum > zinc > manganese > magnesium > copper.

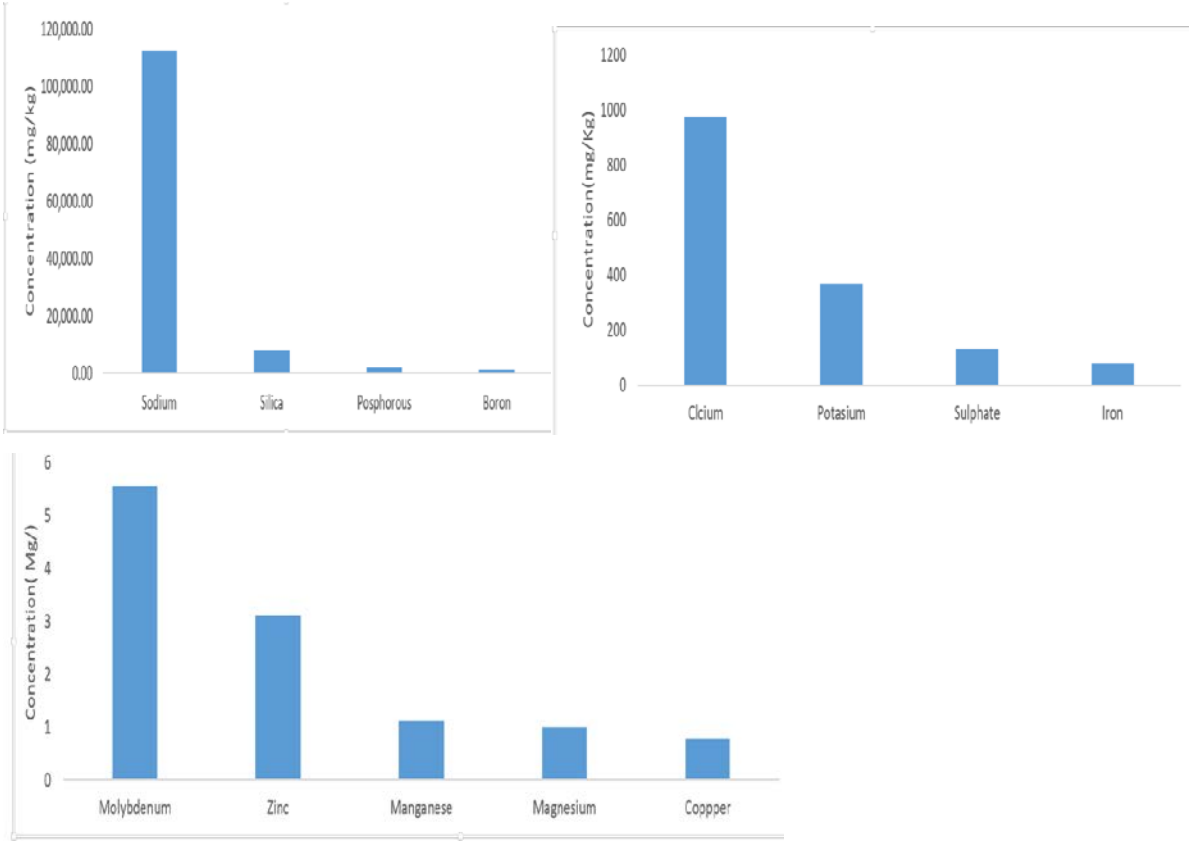


Figure 6. The comparison of the concentration of elements/ ions/compounds in silica samples.

Table 2. Concentration of Elements or ions or compounds (mg/kg,) in silica samples.

Elements	Concentration (mg/Kg)	Elements	Concentration (mg/Kg)
Phosphorus (P)	1,748.41	Zinc (Zn)	3.11
Potassium (K^+)	368.83	Boron (B)	1,293.93
Calcium (Ca^{2+})	976.72	Copper (Cu)	0.78
Magnesium (Mg^{2+})	< 1.008	Molybdenum(Mo)	5.55
Sulphate (SO_4^{2-})	132.45	Sodium (Na)	112,350.00
Iron (Fe)	77.61	Silica (SiO_2)	8,265.21
Manganese (Mn)	< 1.114	Copper (Cu)	0.78

3. 3. Batch Adsorption Studies

3. 3. 1. Effect of pH

The pH is one of the most important environmental factors that affect the adsorbent site. As shown in Figure 7, the pH increased from 2-4,whereas in the range 4-10, the adsorption amount was only slightly affected by pH. The effect of initial pH on bio-adsorption percentage of methylene blue dye was examined over a range of pH values from 2 to 10. The lower and higher removal was observed at pH 2 (65.48%) and pH 10 (95.50%) and Incremental

dye removal was not significant beyond pH 10. For this reason, pH 8 was selected for future equilibrium studies. After adsorption experiments, it was found that at low pH, the dyes become protonated, the electrostatic repulsion between the protonated dyes and positively charged adsorbent sites results in decreased adsorption. Higher adsorption at increased pH may be due to increased protonation by the neutralization of the negative charges at the surface of the adsorbent; which facilitates the diffusion process and provides more active sites for the adsorbent (Neway and Hirpo, 2021). In addition under acidic condition the basic dye is protonated and the intensity of the positive charge is localized more on dye molecules leading to an electrostatic repulsion between adsorbent and adsorbate (Soha and Hossam,2019) as a result it causes a decrease in adsorption capacity.

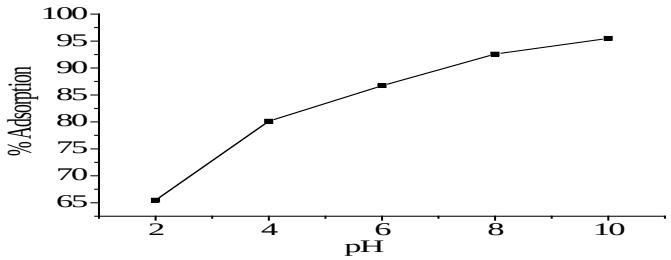


Figure 7. Effect of pH on the removal of methylene blue dye (C_o = 20 mg/L dose = 0.1 g, Volume = 50 ml, contact time = 24 h and λ = 665 nm)

3. 3. 2. Effect of Adsorbent Dose

In order to study the effect of adsorbent mass on the adsorption of methylene blue, a series of adsorption experiments was carried out with different adsorbent dosages at initial dye concentration of 20 mg L^{-1}. Figure 8 shows the effect of adsorbent dose on the removal of methylene blue. Along with the increase of adsorbent dosage from 0.05, 0.1, 0.15, 0.2. 0.4and 0.5g the percentage of dye adsorbed increased from 70.41-98.93% (Figure 8).

The removal increased with increased amount of adsorbent dose up to a maximum efficiency (>95%), after which an increase in adsorbent dosage does not further improve the dye removal, implying that a complete dye removal could not be achieved even though using large amount of the adsorbents. An adsorbent dose of 0.4 g was selected for subsequent studies equilibrium. The increment in removal efficiency of methylene blue day with increase of dose of silica is as a result of the increase in the number of adsorption sites relative to methylene blue day molecules. This can be explained by the presence of a high number of active sites in this mass interval.

Beyond this concentration, the yield becomes constant because the addition of silica gel most likely results in partial agglomeration and thus restricts the active surface area available for dye adsorption (Ingrachen-Brahmi et Al.,2020).

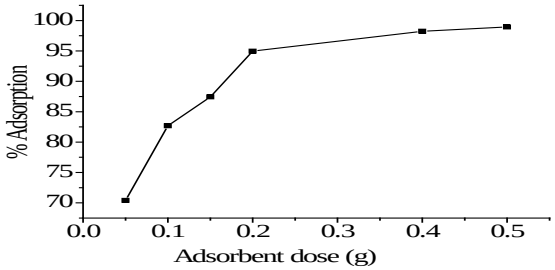


Figure 8. Effect of adsorbent dose on the removal of methylene blue dye at initial (C_o = 20 mg/L, Volume = 50 ml, contact time = 3 h, λ = 665 nm and at optimized pH=10)

3. 3. 3. Effect of Contact Time

The effect of contact time on the adsorption rate of methylene blue is shown in Figure 9 at the time of 30, 60, 90, 120, 150 and 180 minute. To know the time of maximum removal capacity of methylene blue day on silica, the removal of methylene blue day was studied as a function of time by using 0.4 g adsorbent dose (silica) on 20 mg/L initial concentration of methylene blue day solution at pH around 10 in a fixed volume 50mL as shown in Figure 9. The lower and higher adsorption of MB was observed at 30 (76.86%) and 180 (97.82%) minute respectively (Figure 9). The adsorption capacity rate is high at the beginning due to large surface area of adsorbent available for adsorption of methylene blue dye. At the beginning all reaction sites are vacant as a result the removal capacity is high. After the initial rapid adsorption, the adsorption rate was very slow almost reaching a constant value.

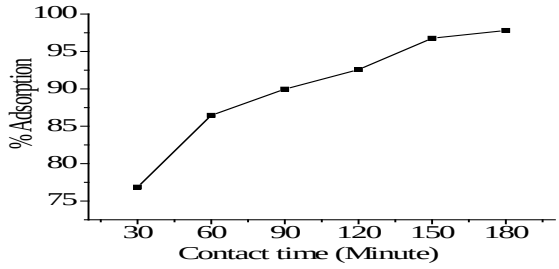


Figure 9. Effect of contact time on the removal of methylene blue dye (C_o = 20 mg/L, Volume = 50 ml, λ = 665 nm, optimized pH=10 and optimized dose =0.4 g)

3. 3 .4. Effect of Concentration

The adsorption of the dyes on MB was studied by varying the carbon concentration (5-40 mg/L). This is attributed to increased weed's surface area and availability of more adsorption sites. It is apparent that the percent removal of methylene blue dye increases rapidly with increase in the concentration of the methylene blue dye weed due to the greater availability of the exchangeable sites or surface area at higher concentration of the sorbent. But it lower decolonization percentage at high dye concentration was reported and it was expected to happen because the inhibitory effects of high dye concentrations which have been observed in this study.

The results are presented in figure 10. From the figure we can say that the uptake of methylene blue dye was rapid at lower concentration (5-10 mg/L) and as concentration increase the amount of methylene blue dye adsorbed was decreased due to the fact that at lower concentration, the ratio of the initial number of methylene blue dye molecules to the available surface area is low and the available sites are high (Eren and Acar, 2006). But at high concentrations of dye, the available sites are fewer as a result the proportion removal of methylene blue dye on silica was lowered from 80 to 71.5. The low and high removal of MB by silica was observed at 40 ppm (71.56%) and 5 ppm (96.35%) (Figure 10). Amount of methylene blue dye adsorbed per unit mass of adsorbent increased with methylene blue dye concentration from 5 to 40 mg/L. Since after a long period of time all the sites are occupied by the methylene blue dye molecules the adsorption become nearly constant whatsoever concentration of day is increased. This suggests forming a monolayer on the acidic silica.

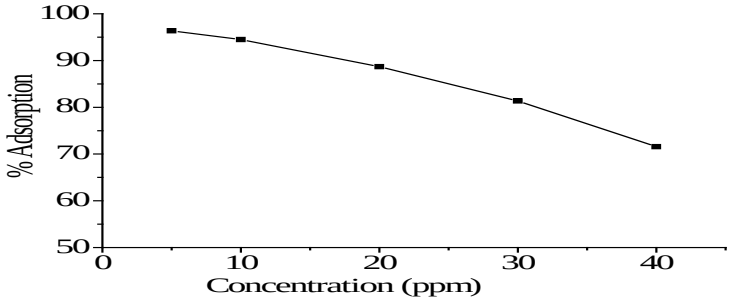


Figure 10. Effect of Concentration on removal of methylene blue dye (C_o = 20 mg/L, Volume = 50 ml, λ = 665 nm, optimized pH=10, dose =0.4 g and time =180 minute)

3. 4. Adsorption Isotherm

Adsorption isotherms are the basic requirements to designing any sorption process and it is defined by specific values, which articulate the surface properties and affinity of the adsorbent.

Adsorption study at equilibrium gives input about the capability of the adsorbent. Equilibrium data can be tested using commonly known adsorption methods Adsorption isotherms used to find the maximum adsorption capacity of the adsorbent. Equilibrium data can be tested by using adsorption methods. Several isotherm models can be used to analyse adsorption data. Among those models Langmuir and Freundlich models are the most common models.

3. 4.1. Langmuir Adsorption Isotherm

According to equation (2.2), the values of Q_o and b were calculated from the slope and the y intercept of the Langmuir plot of C_e / Q_e versus Ce (Langmuir, 1916). From the plot which is shown in Figure 11 below amount the adsorbed for monolayer formation (Q_o), Langmuir adsorption-desorption equilibrium constant (b) and regression constant (R^2) were determined and the values are presented in table below. Table4.1 parameters and correlation coefficient of Langmuir isotherm model for adsorption of methylene blue day on to silica.

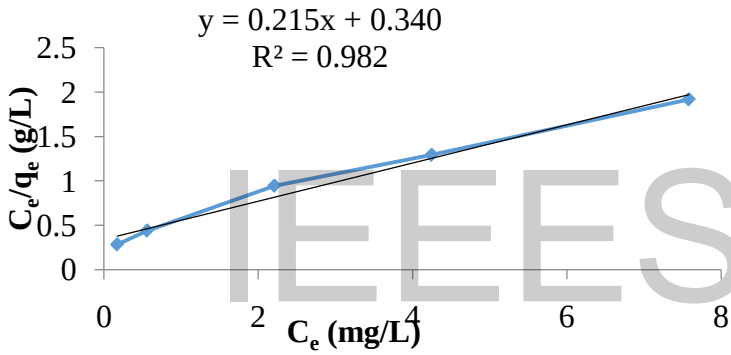


Figure 11. Langmuir plot for adsorption of methylene blue dye on silica (Volume = 50 ml λ = 665 nm, time = 15 min. pH = 10)

The R_L value in this investigation was calculated and it was found to be equal 0.78 which is between 0 and 1 indicating that the methylene blue dye adsorption on silica is favourable.

3.4.2. Freundlich Isotherm for Methylene Blue

The constants K_F and n were determined by using equation (2.4) by plot a graph of log(q_e) vs. log(C_e) (Freundlich, 1907) as shown in Figure below. Freundlich constants K_F and n and regression constant R^2 were determined by and values are shown in the figure

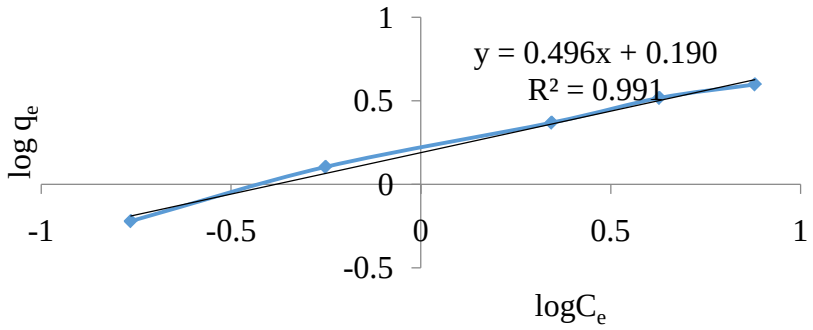


Figure 12. Freundlich plot for adsorption of MB dye on silica. (Volume = 50 ml, λ = 665 nm, time = 15 min. pH = 10)

Table 3. Langmuir and Freundlich isotherm constants for adsorption of methylene blue.

Adsorbent	Adsorbate	Langmuir model				Freundlich model		
Silica	Methylene blue	Q_o(mg/g)	b	R_L	R^2	K_f	N	R^2
		56.5	0.18	0.78	0.98	9.38	1.54	0.99

3.5. Adsorption Kinetics of Methylene Blue Dye on Silica

3. 5.1. Pseudo-first-order Adsorption Kinetics

The adsorption kinetics is quite important in wastewater treatment because it controls the solute removal rate, which in turn controls the residence time of solute uptake at the solid–liquid interface. Actually, adsorption kinetics was one of the most imperative characteristics that signify the adsorption efficiency. The adsorption kinetics process was investigated by various kinetic models such as pseudo–first order, pseudo–second order equations and intra particle diffusion. The pseudo–first order kinetic model is the most popular kinetic equation based on the assumption that the adsorption rate is related to the number of unoccupied adsorptive sites and used only for the rapid initial phase. On the other hand, the adsorption rate could also be approximated by the pseudo–second-order kinetic model. This model is more likely to predict the kinetic behavior of adsorption with chemical sorption being the rate-controlling step (Zare*et al.*, 2014).

Rate constant for the adsorption of methylene blue from the dyeing effluent on adsorbent (silica) was specified depending on pseudo first-order equation . The pseudo first order rate constant was obtained by plotting a liner graph of linear graph of log ($q_e - q_t$) vs. time as shown in Figure below (Lagergren and Vetenskapsakademiens, 1898). If the plot was linear with high correlation coefficient, this indicated that lagergren equation is proper to methylene blue dye adsorption on

silica, so the adsorption process is a pseudo first order. The Lagergren first order rate constant (K_1) and Q_e specified from this model are presented in below with the corresponding correlation coefficient. The calculated Q_e value does not match with the experimental Q_e value Table 4. This pointed that the adsorption of methylene blue dye does not obey the first-order kinetics therefore the pseudo first order model is not used to determine the first order rate constant (K_1) and (Q_e).The results confirm that the kinetics model perfect fit the experimental date with R^2 which equals 0.99.

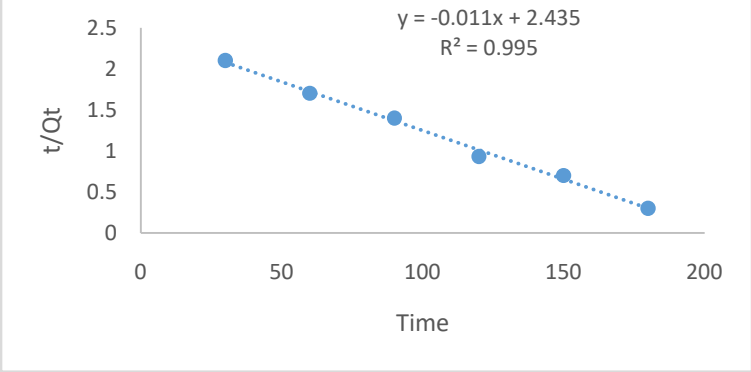


Figure 13.Pseudo-first-order sorption kinetics on silica. (Volume = 50 ml, the Concentration of methylene blue = 20 mg/L, λ = 665 nm, pH = 10, weight of adsorbent = 0.4g)

3. 5. 2. Pseudo-second-order Adsorption Kinetics

The plot of t/Q_t versus time for the corresponding adsorbent is given in Figure 14. Q_e experimental and Q_e calculated values for pseudo second order kinetics model are illustrated in Table 4. It can be observed from that this table that there is an agreement between Q_e experimental and Q_e calculated values for the pseudo second order model.

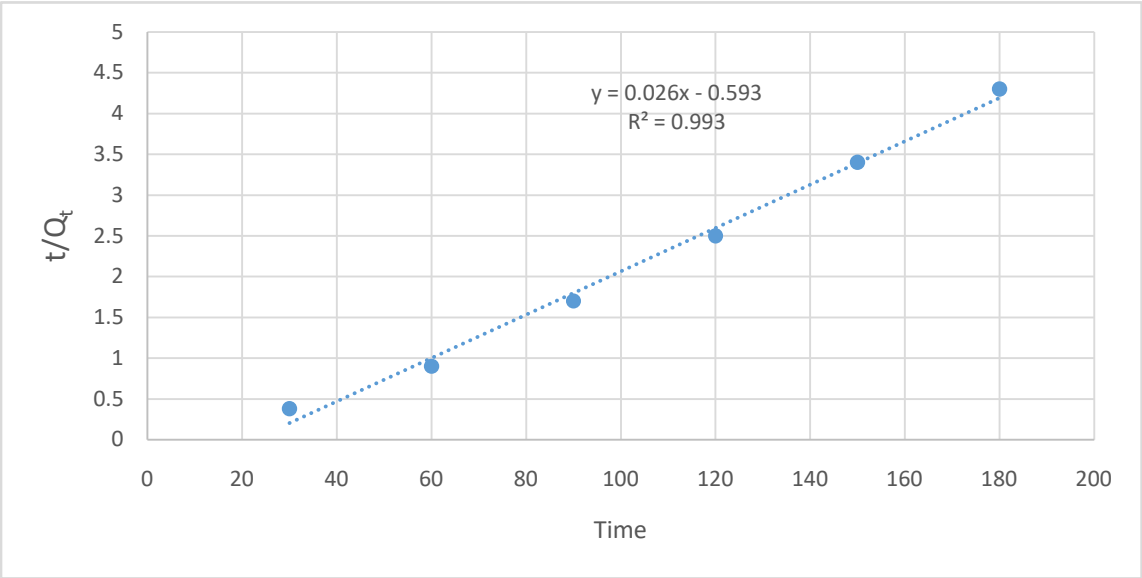


Figure 4. Pseudo second order sorption kinetics on silica. (Volume = 50 ml, the Concentration of methylene blue = 20 mg/L λ = 665 nm, pH = 10, weight of adsorbent = 0.4g).

Table 4. Pseudo first order and Pseudo second order intra-particle diffusion parameters for MB Dye adsorption on to silica

Adsorbent	Q_e (exp) (mg/g)	Pseudo first order			Pseudo second order		
		K_1 (min^{-1})	Q_e (calc) (mg/g)	R^2	K_2(min^{-1})	Q_e (calc) (mg/g)	R^2
Silica	48.87	0.025	12.68	0.99	0.0046	49.87	0.99

4. CONCLUSION

In this study silica was prepared from sorghum stalks. The preparation of a silica from sorghum stalk with effective adsorption capacity of methylene blue dye was studied. The synthesized silica was characterized using the instrument FTIR, PXRD, UV and ICP- OES techniques. XRD confirms the formation of pure phase silica and formation of silica in the composite material and its structure and crystallinity. FTIR spectroscopy analysis was confirmed that the presence of different functional groups onto silica composite and 791.9 cm^{-1} shows formation of Si-O-Si symmetric starching bond. ICP-OES used to determine the element composition of the prepared silica and around 8265.21 (mg/kg) of SiO_2 was obtained. UV spectrometry used to determine the amount of methylene blue adsorbed from aqueous solution using synthesized silica. Furthermore, the results obtained in this study showed good fits to the Langmuir adsorption isotherm, which could suggest a multi sites adsorption process.

Initial concentration of methylene blue, adsorbent dose, pH and contact time were the major factors that affects adsorption of MB by silica were investigated. The adsorption was found to be strongly dependent on pH, contact time, initial methylene blue concentration and adsorbent dose. The uptake of methylene blue by silica was maximal at basic medium (pH 10), lower at acidic region (pH 2-4), and remains significant for neutral pH values. Silica can also be used as a possible alternative for the removal of other dyes from waste water dye because of its multi-functionality. The Langmuir maximum Adsorption (R2= 0.98) capacity Q_m and the R_L value indicate that adsorption of MB dye on to silica is favour. Freundlich model parameters (R^2= 0.99) which fit with Freundlich isotherm. The amount of methylene blue dye adsorbed per gram of silica gel obtained by Lageregren pseudo second order model, Q_e (calc.) value of 56.5 mg/g which was in agreement with the experimental value, Q_e (exp.) indicates that chemisorption may be the rate limiting step where the valance forces are involved by electron sharing or exchange between the adsorbent and the adsorbate.

CONFLICTS OF INTERESTS

The authors stated that no conflicts of interest.

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