



Original Research Article

Using an Agriculture Waster for Eliminating BG from Waste Water

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ABSTRACT

The ability of rice husk (RH) to remove four different types of dye pollutants from wastewater—methylene blue, Congo red, brilliant green, and crystal violet—using various design parameters is the subject of this article. The initial concentration of the dye, the absorbance material packing height, which was RH, the pH of the dye solution feed inlet, the treatment time, the feed flow rate, and the feed temperature were the design parameters studied to adsorb the above four dyes using RH as an adsorbent material. These parameters were varied from (1-100) mg/l, (10-100) cm, (1-8), (1-60) min, (5-100) ml/hr, and (20-55°C). The results demonstrate that for brilliant green, Congo red, crystal violet, and methylene blue dyes from aquatic solution, the highest removal efficiency was (95.81, 93.44, 96.62, and 96.35)%, respectively. and while the removal efficiencies rose with increasing absorption material bed height and feeding temperature, these efficiencies declined with increasing starting concentration and flow rate. For methylene blue, brilliant green, and crystal violet dyes, the removal efficiency rose with rising pH of solution, however it reduced for Congo red dye with increasing pH of solution. The elimination efficiency of the dyes employed in this study's dyes is integrated with all operating parameters to create a general equation using a statistical model. By doing this, we can get rid of agricultural waste RH as well as hazardous dyes that have tainted the water.

Keywords: Brilliant Green, UV-VIS, Ph meter, Methylene blue

Introduction

A coloured organic compound that is chemically attached to a substrate is referred to as a dye. As a result, the substance acquires the appropriate colour and the strength of the chemical connection is increased. Due to their chemical makeup, dyes are non-biodegradable and resistant to some chemical reagents, oxidising reagents, and heat [1]. Chromophores, which create colour, and auxochromes, which work in conjunction with chromophores to make dye molecules soluble in water and improve the fibres' affinity (to connect), are the two main building blocks of dye molecules [2]. Based on the chromophore structures, different dyes can be categorised as acidic, basic, dispersion, reactive, azo, anthraquinone, and diazo dyes. [3]. An organic dye called brilliant green is widely used as an ectoparasiticide and fungicide in the fish farming sector around the world. Aryl methane dyes like brilliant green ($C_{23}H_{5}N_2$) are specifically diamino-triphenylmethanes with the structure depicted in Fig. Karr provides a thorough history of the creation and production of dazzling green (1937). Like most dyes, brilliant green has a variety of names that are synonyms. The dye may be offered under names like Victoria green B or WB, New Victoria green extra O I or II, Diamond green B, BX or P extra, Solid green O, and Light green N. In order to prevent misunderstanding over trade names, [3] assigns each colour a distinct index number and name and provides thorough listings of these synonyms.

The colour CI42040, sometimes known as diamond green and malachite green G, has occasionally caused confusion. Significant amounts of brilliant green are produced for the dyeing of materials including leather, paper, and acrylic fibres. The initial commercial production synthesis yield of brilliant green is about 65%, with possible considerable batch differences. Because of this, dye producers, who are required to create a standard product in terms of its capacity to dye, accomplish this by "diluting" down the dry dye with bulking agents like sodium chloride or sucrose to produce a standard dye strength. Industrial liquid dye strength is typically represented as a percentage of the dyeing capacity of that manufacturer's dry dye, which typically does not include 50% bright green dye. Certainly, a saturated Brilliant green oxalate is found in aqueous solutions in the range of 7–6% [4], although excessive acetic and hydrochloric acid concentrations can result in aqueous solutions exceeding 30%. Even a nominal 100% malachite green dry powder by analysis can only contain 82% (oxalate) or 95% (hydrochloride), the balance of the weight being the acid component. High quality grades of brilliant green can be created by including the additional purification processes in manufacture.

The leuco base is produced by condensing benzaldehyde (1 molecule) with N,N-dimethylaniline (2 molecules) in the presence of strong sulfuric acid (Gr. leuco, colourless). The dye depicted in fig.2 is produced by first oxidising the leuco base with lead peroxide and then subjecting it to hydrochloric acid treatment.

Many of the arylmethane dyes were shown to have potent antibacterial properties early on [5]. They are generally most active against Gram-positive bacteria, less active against Gram-negative bacteria, and least active against bacteria that grow quickly in acid and bacterium spores. There is a wide range of anti-fungal activity in arylmethane dyes. Only the straightforward triphenylmethane forms of the arylmethane dye have significant antibacterial action. Therefore, patent blue and wool green S are not very efficient fungicides, while malachite green, dazzling green, victoria green, and crystal violet are [6]. Malachite green, bright green, and crystal violet are generally the only colours that have been used as antimicrobials because they are all powerful at very low doses. On the ecosystem of the water supply and the entire environment, cationic dyes are the most toxic and destructive. Because of their chemical stability and cancer-causing and mutagenic effects on oceanic biota by obstructing light from penetrating the water, which slows down photosynthetic activity, as well as their propensity to contaminate fish and other organisms due to chelating metal ions, the release of such toxic dyes into the environment has become a global concern. These dyes can produce harmful compounds when they are oxidised or reduced in water, which makes wastewater treatment necessary. When used as food additives, they also result in hyperactivity, low frustration tolerance, impulsivity, and lack of focus. To remove organic contaminants, a variety of techniques have been tried, including chemical oxidation, electrolysis, coagulation, ozonation, reverse osmosis, ultra-chemical, filtration, ion exchange, precipitation, biological approaches, and many others. BG produces discomfort in the digestive system, which results in nausea, vomiting, and diarrhoea. Additionally, it causes coughing and breathing difficulties in the respiratory system. Additionally, it can irritate skin, resulting in redness and pain upon close touch. Adsorption methods may be divided into batch, which is a straightforward method that provides a practical approach to explain the parameters that affect the adsorption process, and continuous, which is helpful in determining the amount of adsorbent needed to remove the contaminants from wastewater. The dye analysis examines a sample from other artefacts as well as reference dye material. Liquid chromatography is used for it. Typically connected with mass and a diode array detectors for spectrometers (LC/DAD/MS). the captures the chromatograph's picture from both detectors (absorbance at one of the wavelengths, total ion,

base peak or extracted ion chromatography). Additionally shown is a UV visible spectrum image. the mass spectra of Mass spectra from multistage mass spectrometry (MS/MS) are given, providing information on the molecular ion's fragmentation.

Table: Properties of Brilliant Green Dye

| | |
|---------------------|---|
| Physical State | Green Crystal powder |
| Melting point | 164 0C |
| Solubility in water | Soluble |
| Odour | Less |
| Molecular weight | 927.03 |
| Polymerization | Will not occur |
| Toxic effect | Causes skin irritation and eye irritation |
| Stability | stable |

Literature Review

2013's Firoos Saeed Abbas [7] In this work, the author investigates the effectiveness of rice husk (RS) in removing the dye brilliant green. An agricultural waste that functions as an adsorbent is rice husk. The simulated synthetic aqueous solution (SSAS) of dye concentration is used to conduct this study. For this, a number of parameters are measured, including the initial dye concentration, the height at which the adsorbent material was packed (RH), the pH of the dye solution feed intake, temperature time, feed flow rate, and feed temperature. In ideal circumstances, these values are 1 mg/L, 2.54 cm ID, 150 cm height, 1-8, 1-60 min, 5-100 ml/min, and 20-55 °C. The sorption column, which is used for this experiment, is filled with absorbent medium to a height of 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 cm. To avoid air bubbles, the column is then cleaned with double-distilled water before being run with the dye at the specified flow rate, concentration, and pH. R Laxmipathy (2014) [8] uses the spectrophotometer thermogenesis 10UV, USA, to characterise the adsorptive capacity, which accounts for 95.81% of the BG. In order to get rid of the dangerous, toxic brilliant green dye, this paper uses watermelon (WR) and activated watermelon rind (AWR), which are inexpensive and environmentally benign adsorbents. This was prepared by subjecting it to a 1:1 phosphoric acid treatment. The watermelon peels were chopped into pieces, washed, and dried outside for seven days. They were then washed in hot water and dried for 48 hours in an oven set to 85°C. Then it was crushed and sieved through a mesh size of 100. After being activated for 4 hours at 110°C, WR is treated with 1:1 phosphoric acid. After washing it twice with distilled water to get rid of the extra acid, it was dried for two hours at 110°C. WR and AWR are then prepared for sorption. In the process of removing dye, a number of other factors

are also necessary and crucial, including pH, the impact of adsorbent dose, the impact of contact time, and dye concentration. Some methods, such as FTIR spectroscopy, are utilised to characterise WR and AWR and identify the functional group. The morphology of native and activated WR was investigated using a scanning electron microscope (SEM). Adsorbent dose is 1.5g/L, starting concentration was 50mg/L, and contact period is 60min at 303K are the parameters for optimal adsorption. To remove BG dye from an aqueous solution, M.K. Daheri (2017) [9] employed trap peels (TP) and trap peels that had been treated by oxalic acid. In the adsorption of BG onto TP, functional groups like carboxyl, hydroxyl, and amino were active. There were other factors at play, including the impact of pH, contact time, ionic strength, starting dye concentration, and temperature. Characterization carried out only using FTIR. pH is 3.61, temperature is 60°C–70°C, and contact period is 240 min. Siddra Farooq (2018) [10] combines solanum tubero (ST) peels and agricultural waste must ruminant (MA) for cost-effective sorptive removal of vivid green dye in an environmentally acceptable manner.

For isothermal and kinetic inquiry, the optimal conditions of temperature, pH, and biosorbent dosage were adopted. Which demonstrates that MA peels with an adsorptive capacity of 10.74 mg/g were able to absorb more BG dye. the SEM and FTIR characterization. The ideal pH for MA and ST peels is 6, and the recommended adsorbent dose is between 0.2 and 2.0 g, with a contact period of 60 minutes at 10°C. Ramis, EmanS. (2018) [11] The author's goal in this research is to employ readily available, inexpensive commercial green adsorbent to remove vivid green dye from aqueous solution. As a green adsorbent, rice straw (RS) and rice straw ash (RSA) are employed. These adsorbent's capability is researched. Different factors, such as dye concentration, contact time, and adsorbent dosage, are used to carry out the adsorption. This was conducted utilising the Langmuir, Freundlich, and Temkin absorption isotherm. SEM and FTIR are used to analyse the adsorption data and morphology of the adsorbent. The adsorbent (RS) was purchased from a farm and properly cleaned with water to eliminate all dirt and soluble material. It was then dried at 105°C, crushed into RS, and the remaining portion was burned to ash at 600°C in a muffle furnace (RSA). The parameters under study include contact duration (30 min for RS and 60 min for RSA), adsorbent dose (5 mg/L at room temperature with steady shaking of 200 rpm), and dye concentration (20 mg/L to 100 mg/L) for the removal of BG dye. RS saw a reduction in removal percentage from 88.42 to 52.76% while RSA had a reduction from 89.25 to 78.63%.

This research by Miyah Youssef (2019) [12] aims to identify a natural adsorbent that is both efficient and affordable. In order to get rid of the BG and EBT colours, the author uses bagasse (BS) as a bio sorbent. These tests need the study of a few factors that are crucial for the removal of dyes and the completion of characterization. Therefore, these characteristics include the impact of contact time, initial concentration, dosage, and temperature. SEM and FTIR are characterising methods used to investigate the adsorbent for information on shape and functional groups both before and after adsorption. The adsorption is done in a batch reactor while a beaker holding 200ml of coloured solution is being stirred. Every five minutes, a sample was obtained, the dyed solution was separated from the BS by interacting with a syringe filter with 0.45 micro holes, and the concentration of BG and EBT was then calculated. 520nm and 625nm measurements of the adsorbent, respectively. using a spectrophotometer for UV-visible light. The contact time is 60 minutes for the parameters when they are at their best.greatest absorption. For BG and EBT, the effect of an adsorbent dose is 40 mg/L and 20 mg/L, respectively. The temperature ranges from 20° to 60°C. According to the study on adsorption kinetics, the pseudosecond-order kinetic model more accurately captures the adsorption data for dyes. John M. Cardva(2020)[13].

In this review the author is aiming to dye brilliant green by using low-cost agricultural waste which was a cocoa pod husk(CPH) biochar. In this, the biochar was treated in two steps of activation with NaOH. In the first step, it was dried at 110°C for 18 hrs and then ground and sieved size between 350 to 500 micrometres, h 1M NaOH and dried in an oven at 90°C for 12hrs sis rinsed were repeated for the second step also with slight modification. In this CPH powder is heated to 350°C for 1hrs but in the previous step, it was 550 °C. There are certain parameters which are very important to study the adsorbent in optimum conditions like pH, contact time, adsorbent dose, and concentration of dye.

These optimum conditions are like, the pH range which varies from 3to10 and the optimum for BG dye is 6 due to the adsorption mechanism. The concentration of dye is 10mg/L. The optimum adsorbent dose is 10 mg. There are various characterization techniques which are also used to better understand the adsorbent. The FESEM is used to look over the surface and FTIR is used to look over functional groups, NMR, XRD and BET are also used to characterise and see the best results. Kamal sukla Baidya (2020) [14].

In this literature author uses agricultural waste as an adsorbent to remove brilliant green dye which is areca nut husk (ANH). Which is chemically treated first and then used as adsorbent.

To do this experiment various parameters is necessary to be observed like the pH, adsorbent dose, initial concentration, speed at which rotation work and the temperature after that some techniques were also used for the surface characterization and elemental composition of adsorbent (ANH). These are SEM and energy-dispersive X-Ray (EDX). From there, the author observed the changes in the surface of the adsorbent like the removal of natural wax etc. FTIR spectroscopy indicates the presence of functional groups(-OH), (-C=O), (C=C) and (COOH). The optimum removal of dye is 97% in optimum pH 7, the adsorbent dose is 10g/L, initial concentration 100mg/L at an agitation speed of 200rpm at 298K temperature and contact time 30min. Kalid Ansari (2020) [15] uses lawsania inermis seeds (CTLISP) as adsorbent for removal of BG dye. The adsorbent was characterized by various techniques such as FTIR, EDX, SEM and TEM. Effects of various parameters such as concentration, pH, doses, contact time was carried out. Maximum adsorptive capacity 34.96 mg/g at 50°C. Optimised pH is 6, contact time is 180 min, effect of adsorbent dose is 0.1-1.0g. Balender Shekhar Giri (2020) [16] uses corncob biochar (CCBC). Characterization by FTIR spectroscopy, SEM, XRD and BET analysis. This study is carried out at different optimum parameters contact time is 180min initial dye concentration is 50ppm, the adsorbent dose is 2.0g, effect of temperature is 318K. R.M. Jugade (2020) [17] uses used tea powder for the removal of BG dye from aqueous solution. Pore morphology, surface properties, crystalline nature and thermal stability of (UTP) were analysed by using SEM, FTIR, XRD, and TGA analysis. The optimized working parameters were found to be pH 6, UTP does 100mg, adsorption time 60min and dye concentration 100mg/L. The maximum adsorptive capacity is 101.01mg/g. Muhammad Sadiq Hussain (2021) [18] uses trapa natans peels (TNPs) and Citrullus Lantus peels (CLPs) were used as adsorbent to removal of BG dye from aqueous solution. Characterization and surface morphology were studied by FITR and SEM. The various optimum parameter is for (TNPs) adsorbent were adsorbent dose 0.8g, contact time 25min, initial pH 5, temperature 30°C and agitation speed 100rpm. For (CA-CLPs) adsorbent dose 0.8g, contact time 20min, pH 5, temperature 30°C and agitation speed 100rpm. SAGAM. BADR (2021) [19] This literature review is also based on an adsorbent which is a agricultural waste. Which is also abundantly available and low cost. So, the author is used watermelon peel as an adsorbent for the removal of coloured effluent which consist of dye like BG. The removal of dye effects different parameters like pH of dye solution, contact time, bio sorbent dose, initial concentration if dye. The characterization of adsorbent is also done before and after brilliant green dye removal with different techniques like surface and composition by (SBET), FTIR, SEM, and SPM. The

sorbent is washed several times with tap water and dried then wash with hot water and dry for 48hrs at 85°C and ground as sieved through 100mesh. So, the various above-mentioned parameters in optimum condition are as follows- pH is 8, the adsorptive capacity is increased by 98.40%, and the influence of contact time is 6.2mg/g between 10min to 60min. The optimum bio-sorbent dose is 0.8g/100ml. The initial BG dye concentration is 10-100mg/L. Ramadan Abd El-Ghani Mansour (2021) [20] In this paper the author used carbon derived from date pits (ADPC) for the removal of BG from aqueous solution as a green absorbent. The raw date pit collected from farm and washed with boiled water to remove any kind of residue. Pits were dried to 110°C in electric oven to make them moisture free then ground to a fine powder. Then add concentrate phosphoric acid (85%) into container having date pits powder until 20g seeds will be impregnated in 40ml of phosphoric acid at 25°C for 24hrs. Then the soaked seed were dried at 110°C for 1 hrs. Then seeds placed in muffle furnace for 2hrs. Then neutralize it with hot distilled water and was dried at 110°C for 3hrs and finally sieved to 75 micro meter diameter. The characterization is of adsorbent is carried out by using SEM to study morphology of (ADPC) before and after adsorption of BG. EDXS analysis was used to clarify the qualitative elemental composition of activated date pit carbon (ADPC) before and after adsorption of BG dye and FTIR analysis was used to see how far the molecular structure of (ADPC) has been changed after adsorption of BG dye. There are several parameters which affect the adsorption, the initial dye concentration 10-50ppm, the contact time 55min, 0.6g optimum adsorbent dose at 25°C and at optimum pH is 8. The kinetics which was best fitted was pseudo second order model. Hem Lata (2006) [21] uses parthenium heterophorias (PH) which are unwanted weed for removal of BG dye from aqueous solution. The characterization techniques used is SEM and FTIR and optimum parameters are initial concentration is 50mg/L, the pH is 7 and adsorbent dose is 1.0g/100ml.

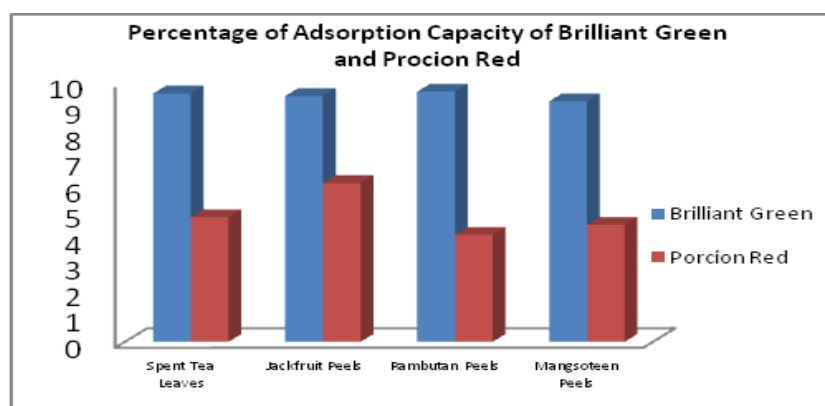


Figure 1: Percentage of adsorption capacity of brilliant green and procion red

Materials and Methodology

The following chemicals and reagent used during the study are: Brilliant Green dye Hydrochloric acid (HCl), Sodium hydroxide (NaOH), Distilled water. The study was performed using the following instruments: Double beam UV-Visible spectrophotometer (Shimadzu, model-1800), Analytical Balance Mettler-Toledo ME204 (Pocklington, United Kingdom), Contech LAB pH meter (Model pH-103, Mumbai, India), Filter paper (Whatman 42), Laboratory Incubator, and Analytical shaker, magnetic stirrer and Ultrasonic Bath from PCI Analytics (Mumbai, India).

Preparation Of Adsorbent

An agricultural adsorbent which is a fine powder was sieved through a sieve shaker of ASTM No. 32 as shown in fig.3. Very fine powder was obtained which was further used to study. Then the adsorbent was washed thoroughly with distilled water to remove all dust and dirt with 1:5 ratio of water and adsorbent up to the filtrate gets clear as shown. After that the adsorbent is kept for air dry for 24 hrs. Then kept it in incubator at 100°C for 12 hrs. and crushed with help of pestle mortar.



Fig 2: Adsorbent



Fig 3: Air dry Adsorbent

Treatment of adsorbent with acid (HCl) and base (NaOH) and neutral 0.1M NaOH and 0.1 M HCl was prepared.

5gm of adsorbent powder was mixed with 50ml of (0.1M) HCl. 5gm of adsorbent powder was mixed with 50ml of (0.1M) NaOH. The prepared solution was then kept on a magnetic stirrer for 2hrs then left for 24 hrs in the solution. The solution of base treated was filtered and washed with distilled water until the adsorbent gets neutralised. The acid treated adsorbent also filtered and wash thoroughly until it gets neutralised. The pH was measured for both acid and base treated adsorbent before and after each washing. It was 5.6 and 8 respectively before and 7 after for both acid and base treated water sample. Then again acid, base and neutral treated adsorbent is kept in incubator at 100°C for 12hrs. In the end it was crushed with help of pestle mortar.

Preparation of stock solution of Brilliant Green Dye Taken volumetric flask and filled it with 50ml of distilled water.

Measured 1mg of brilliant green dye with the help of a weighing machine. Now mix that 1mg brilliant green dye into 50 ml volumetric flask and add minimum amount of water. The volume was finally made up to 50 ml with distilled water. The solution was shaken properly. The stock solution of brilliant green dye was prepared.

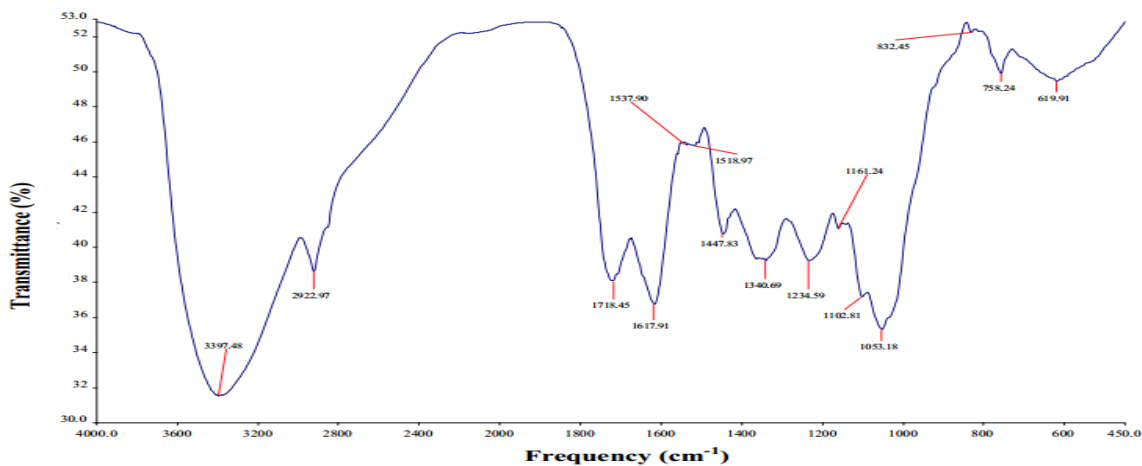
Standard sample preparation

30 mg of acid treated, base treated and neutral adsorbent weighed with the help of weighing machine and put them in separate test tubes. 3 mL of brilliant green dye solution was measured and mixed with 30mg of the adsorbent which were treated with acid, base and neutral adsorbent. Shake each test tube for 45 minutes with the help of an analytical sonicator.

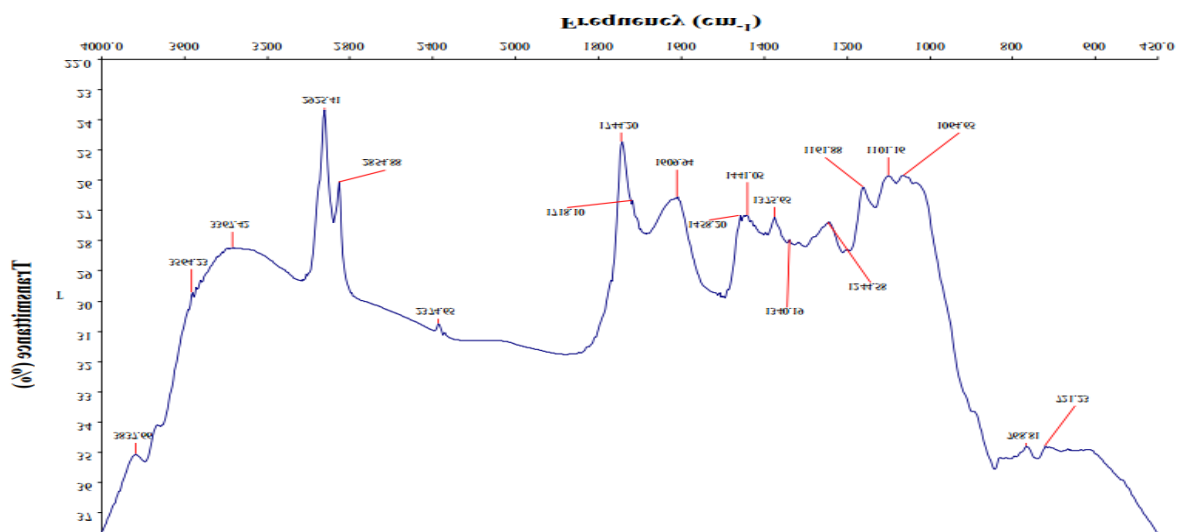
Result and Discussion: Standard Adsorbent UV Visible Spectrometer Analysis, First, a blank sample of water-treated adsorbent was put through the UV-Vis spectrophotometer to establish a baseline. Then, the solution of acid- and base-treated adsorbents with vivid green dye was added, and the spectrophotometer was used to get spectra in spectrum mode. On the basis of the spectrum produced, the highest absorbance of brilliant green (BG) can be seen in Fig. A's typical UV spectrum. Similar to that, Figure B. shows the UV spectrum of BG adsorbed in neutral medium. When comparing the spectrum to the usual brilliant green spectrum, it is

evident that neutral adsorbent causes the absorbance to drop, meaning the dye is absorbed by the adsorbent which is neutral in nature. Again, following the steps, the UV spectrum of brilliant green (BG) in NaOH (basic medium) can be seen in fig. C and on the basis of spectrum obtained it shows absorbance is further decreased when compared with standard spectrum. The maximum adsorption is seen in acidic treated adsorbent which is lowest as compared to standard curve of BG.

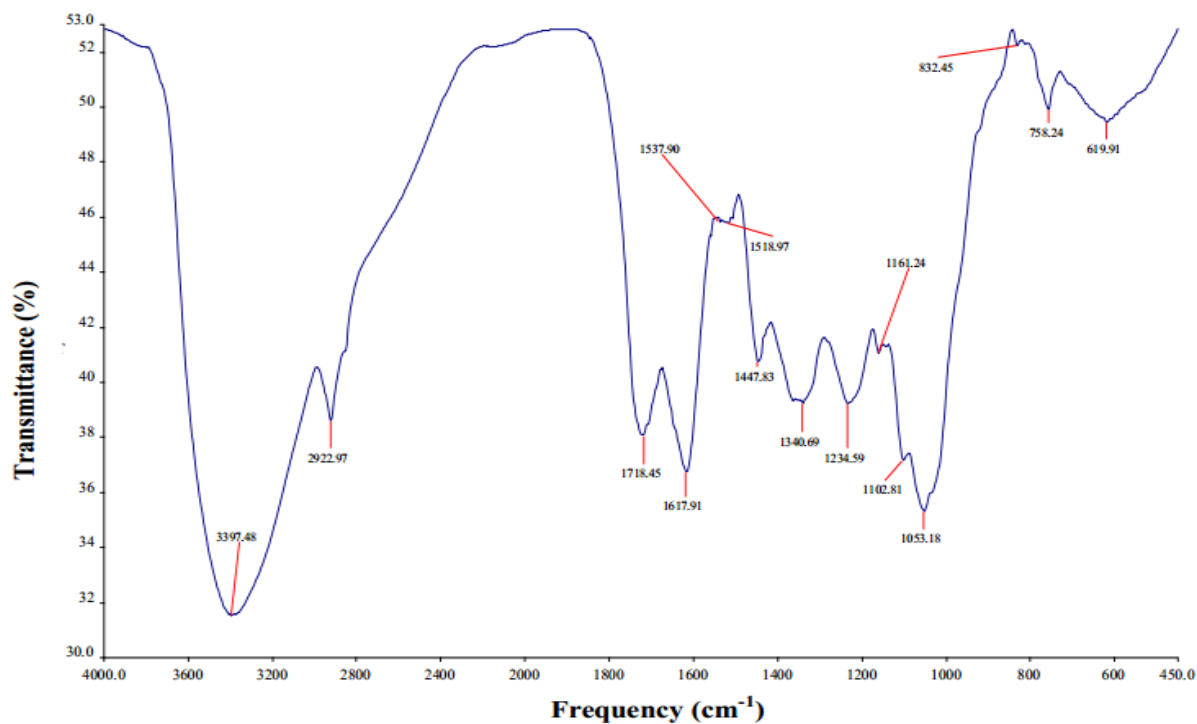
The sample report is slightly showing different results from the standard report of brilliant green. In this the treated adsorbent with water, acid and base at different concentration of 1.438, 2.298 and 1.345 respectively of brilliant green shows the maximum adsorption with acid treated adsorbent which is 0.273 mg/g at 625nm. This indicates that there are electrostatic interaction between adsorbent and dye.



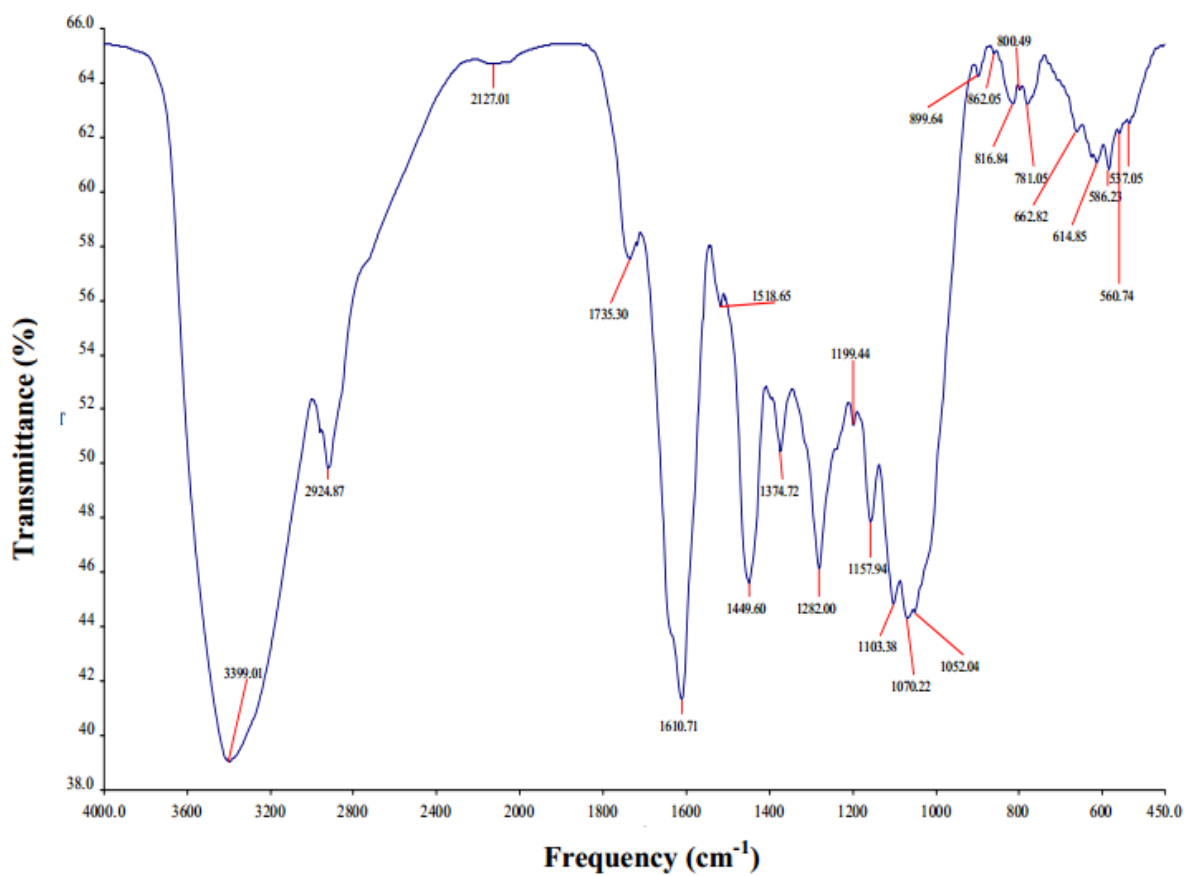
(A)



(B)



(C)



(D)

With the extrapolation of the standard graph comparing the data of the sample the removal efficiency of the brilliant green dye is found to be

The initial dye conc. = 20ppm

Dye conc after removal = % removal = (initial conc – final conc)/(final conc) * 100

With the data and formula above removal efficiency was found to be –

Effect of pH: The adsorption of the dye was highly dependent on the pH of the surface of adsorbent and ionisation degree of adsorbate functional group. The pH is varied from 3 to 10, dye concentration is 3mg/30ml at room temperature with agitation speed of 200rpm. The removal of dyes is increased as the pH decreases.

Conclusion

From the research presented here, it can be inferred that agricultural waste can be used as an efficient adsorbent for the removal of Brilliant Green (BG) from waste water. The adsorbent is processed in various media, including acidic, basic, and neutral solutions. The reference and treated dye samples were analysed using a UV-visible spectrophotometer for this study. Information about the variance in bright green absorbance in various media is provided by the absorption spectrum. In an acidic media, the greatest absorption is observed. Thus, it can be concluded that adsorbent that has been treated with an acidic medium is particularly effective at removing Brilliant Green Dye.

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