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Ulva Lactuca Algae as an Adsorbent for Adsorption of Methylene Blue from Dye Industry Waste Water

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ABSTRACT

Dye industry is one of the major contributors of India's economy and has been growing gradually. As much as it contributes for economy it's also contributes for water pollution, dye industry produces high amounts of effluents, they consist chemicals and color pigments like Methylene blue. Methylene blue is one of the type of cationic dye that is environmentally toxic.it is a synthetic dye mainly used for dyeing fabrics and leathers etc.. Removal of these pollutants is an important consideration for the industries. Removal of these pollutants can be done in various ways, however adsorption is the prominent method for removal of the these pollutants. Removal of these pollutants is an important consideration for the industries. Removal of these pollutants can be done in various ways, however adsorption is the prominent method for removal as it is efficient and less complicated than other methods. Where the adsorbents used are usually based on chemicals and a very low percentage of adsorbent is based on algae. This report is an attempt to explore the possible advantages of an adsorbent developed from algae mainly from Ulva Lactuca. In this report an adsorbent produced from Ulva Lactuca was tested for removal of Methylene blue solution of different concentrations. The algae bio mass used in this report is a specie of ulva lactuca which is widely available in sea shores of Visakhapatnam. The adsorption capacity of the adsorbent sample was determined. The test determined that the adsorbent from the Ulva Lactuca has a potential that needs to be explored. This report provides important insights on the algae as an adsorbent.

***Keywords*:** Ulva Lactuca; Methylene Blue; Effluents; Adsorption.

1. INTRODUCTION

1.0 Introduction to Dye

Environmental problems as a result of dye house effluents because of the toxicity of the dyes and the improper handling of such refuse, many industrial employees are emerging skin illnesses and respiratory issues. The discharge of dye-containing effluents into the water environment is particularly undesirable due to their color, which is harmful, carcinogenic, or mutagenic to life forms, mostly due to carcinogens such as benzidine, naphthalene, and other aromatic compounds. A substantial percentage of industrial activities release pollutants into the environment. The industry's severe environmental problem has been identified as gaseous emissions. Despite much conjecture about the amounts and types of air pollutants emitted by textile operations, air pollution data for textile manufacturing operations are difficult to obtain. The textile industry uses a significant amount of water in its manufacturing processes, primarily in the dyeing and finishing activities of the factories. Factory wastewater is regarded the most polluting of all manufacturing sectors, especially in terms of quantity and effluent composition. Unfortunately, due to their high resilience to light, temperature, water, detergents, chemicals, soap, and other factors like bleach and perspiration, most dyes bypass standard wastewater treatment techniques and remain in the environment. Dyes have high thermal and photo stability and can resist biodegradation for a long time in the environment. The parameters of water to be checked for pollution are,

- PH
- Temperature
- Alkalinity
- Dissolved oxygen (DO)
- Electrical conductivity
- Total dissolved solids (TDS)
- Total suspended solids (TSS)

- Total hardness
- Chemical oxygen demand (COD)
- Total solids (TS)

The biggest environmental concern with dyes is their absorption and reflection of sunlight that goes into the water. Light absorption reduces the photosynthesis process of algae and has a significant impact on the food chain. Many dyes and the byproducts of their decomposition are harmful to life, mutagenic, or carcinogenic. Industrial effluents mostly release dyes into the environment. The quality and transparency of water bodies like lakes, rivers, and others are significantly impacted by the presence of extremely minute volumes of water that are yet clearly visible, which harms the aquatic ecology. Due to the dyes' significant toxicity and mutagenicity, light penetration and photosynthetic activity are reduced, leading to an oxygen shortage and limiting downstream beneficial uses including irrigation, drinking water, and recreation. Even it until middle of the 19th century, all dyes used for fabrics were made naturally until Perkin invented Mauvin in 1856. Ever since, there has been no turning back in the development of synthesis dyes owing to their affordability, wide availability of colors, high dyeability, and most importantly simplicity of production. The textile industry uses and produces 1.3 million tonnes of dyes and pigments, the bulk of that being synthetic. The textile industry, one of the largest in the world, generates an incredible 60 billion kgs fabric annually and uses up to 9 trillion gallons of water. During the dyeing process, 10–25% of textile dyes are wasted, and 2–20% are released as aqueous effluents into other environmental elements. sources of dye house effluents are Pharmaceutical, cosmetic, food, paper, leather, and paint industries as well as textile and pharmaceutical industries. several colored ingredients are employed by the dye house industries: Azo dyes make up the majority of all colorants in terms of quantity and manufacturing, accounting for 60–70% of all organic dyes produced globally. At 1500000 tonnes in 2014, market demand for dye and dye intermediates is anticipated to increase. At the moment, India makes up around 6% of the worldwide market. Methylene blue, Malachite green, Rhodamine - B, Dyes, Astrazone blue, Maxillon red, Teflon blue, Methyl Violet, Water soluble dyes, Aniline blue, Congo red, Crystal violet, Naphthol blue black, Safranine - O, Basic dyes, Basic blue 3, Basic red 22, Basic black 9.

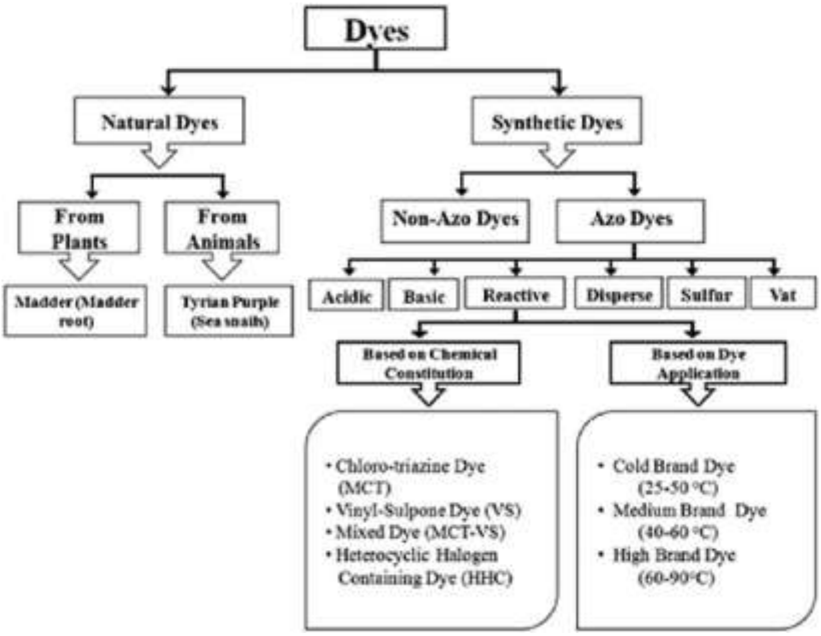

Fig.1. Types of dyes

(Source: https://www.researchgate.net/figure/Flow-chart-indicating-dye-classification-on-the-basis-of-dye-chemical-constitution-and_fig1_299475381)

2. REVIEW OF LITERATURE

2.0. Literature Review

Mohamad et al. In this paper they have used teak wood based activated carbon via response surface methodology to adsorb remazol brilliant blue dye. They have prepared the teak wood based activated carbon by collecting chips from furniture manufacturing factory and activated by drying and carbonized at the temperature of 550°c for 1hr.They have studied the batch adsorption studies and simulates the mass transfer process using polymath software. They have described the kinetic data using the polymath mass transfer software.it has shown that the adsorbent have high actual mesopores surface area of 983.23m^2 /g .[1]

Shirinafshin et al. have used activated carbon derived from filamentous algae to adsorb basic blue 41 (BB41) dye. The adsorbent achieved a 94% removal of dye at concentration of 100mg /l at. pH 9 using 1g/l of adsorbent at a contact time of 90 min. They have prepared the adsorbent by collecting the algae, drying it and powdered to size 100 meshes. Activation of the algae powder were done by adding of phosphoric acid with 3:1 ratio and soak time for on hour .the product is placed in an electric furnace for 3h at 650°c in a nitrogen flow rate of 94.4 ml /min .the powder is also washed with HCl ,hot water and distilled water respectively, they dried it an oven for 2h at 105°c .then the final activated carbon samples were achieved and crushed ,sieved in mesh size 100 and adsorbent is used for the experimental.[2]

Kim et al. have used pine saw dust bio chars (PSB) and post modified PSB with mg/Al layered double hydroxides to adsorb the azo dyes, methyl orange, sunset yellow (SYF). They have studied and investigated the adsorption capacities of two types of adsorbents and compared both of them. They have concluded that the adsorption of azo dyes is higher through the post modification of pine saw dust - based bio chars which are modified and also have higher efficiencies of methyl orange and SYF compared to other bio chars and have high regeneration efficiency. [3]

Soleimani H. et al. have used a modified acidic pumic stone to adsorb remazol black B (RBB) from aqueous solutions and investigated the adsorption capacity of the adsorbent .the adsorbent preparation is done by adding various acids like acetic ,sulfuric , phosphoric,nitirc and hydrochloric acid to the pumic stone .they have observed that the modified pumic stone given more adsorption capacity (10mg/g) in removal of RBB then for raw pumice (5.26mg/g) .they have concluded that pumic stone modified with various acids will give high efficiency in removing the RBB from industry effluent than using the raw pumic stone.[4]

Wanyonyi et al. used dried roots of Eichhornia crassipes were used to study the adsorption of Congo red (CR) from aqueous solution. For the sake of sorption kinetics and isotherms, batch tests were conducted. Adsorption process was strongly reliant on contact time, adsorbent dosage, starting dye concentration, and particle size, according to experimental data. Within 90 minutes, E. crassipes (roots) attained the sorption equilibrium for Congo red dye with an adsorption efficiency of up to 96%. The equilibrium parameters could best be determined using the Freundlich isotherm model, while the sorption kinetics followed a pseudo-second-order kinetic model. These findings showed that E. crassipes roots are a useful, inexpensive, and ecologically acceptable biomaterial for removing dye from aqueous dye solutions and industrial effluents.[5]

Husien et al. have prepared four types of adsorbents which consists of raw algae, physical activated carbon, H_3Po_4 chemical activated carbon and the commercial activated carbon and studied and compared the adsorption capacities of methyl orange. They have characterized the adsorbents using Fourier transform infrared (FTI-R) ,X-ray diffraction and scanning electron microscope (SEM) . Results shows that maximum general efficiency is achieved at nearly 250 ppm for all the adsorbents used.[6]

Sartape et al. have used limonia acidissima (wood apple) shell as an adsorbent to adsorb the malachite green (MG) dye from aqueous solution .they have characterized the adsorbent before and after the adsorption using FETR ,SEM analysis .they have used larger greens model for prediction of systems kinetics and interparticle diffusion study and Boyd plot were used for the study of mechanistic .the results shows that 98.87% efficiency for removal of MG dye with initial concentration 100mg/L at pH 7-9 .they have concluded that wood apple shell is a economically low cost adsorbent as compared to other adsorbents which are used to adsorb malachite green from aqueous solution.[7]

Praipipat P. et al. have used chicken egg shell beads (CB) ,duck egg shell beads (DB) mixed iron ,oxide hydroxide (CBF) ,oxide hydroxide (DBF) chicken egg shell beads ,mixed zinc oxide (CBZ) and duck egg shell beads were synthesized to adsorb reactive 4blue dye .they have used various characterized techniques such as XRD , FESEM -FIB ,EDX and FTIR were used to identify the crystalline structure ,surface morphology and chemical composition and functional groups .they have used frendlich and pseudo second order kinetic models to explain the adsorption patterns .they have stated that the increase in temperature was not favourable for RB4 adsorption on to dye adsorbent materials .they have concluded that all dye adsorbent materials given above are potential materials for RB4 dye adsorption solution in an aqueous solution and they can use in industrial applications.[8]

Tadele Assefe A. et al. have synthesized three types of kaolin based adsorbents (benificiated , raw powder and calcined) to adsorb the basic yellow (BY28) dye from aqueous solution. The % removal of efficiency of basic yellow 28 dye were obtained as 94.79 % for beneficiated, 92.08% for raw powder and 87.08% for calcined kaolin adsorbents at an initial concentration of 20mg/l , pseudo second order models to describe the kinetics in the adsorption process .they have used several isotherms like Langmuir and Freundlich for the kinetic study .they have concluded that all the adsorbents prepared from kaolin were examined for effective removal of basic yellow BY28 dye.[9]

Vij R. et al. have done a batch and column study of adsorption. They have synthesized hydrilla verticillata biomass as an adsorbent to adsorb reactive red dye 120 from simulated waste water .their study reveals that increase in temperature results in more diffusion of dye molecules in to the internal pores of the verticillate and indicates that the process is an endothermic. Pseudo second order kinetic models are suited for the above experimental. they have concluded that H .Verticilla biomass is an effective biomass for the removal of reactive dye RR 120 .[10]

For dye removal throughout the recent times, a variety of physical, chemical, and biological techniques have been used, including membrane filtration, ozonation, photo-catalytic degradation, electrochemical, ion exchange, and adsorption. Adsorption is the most efficient separation technique for the adsorption of organic dyes and other pollutants in waste water among them because it is inexpensive, convenient, easy to use, has a straightforward design, and produces no secondary contamination. Lately, many adsorbents, including activated carbon, inorganic oxides, zeolites, clay minerals, etc., have been widely used to remove dyes. These adsorbents' weak characteristics, such as low adsorption capacity, poor selectivity, and weak regeneration, however, restrict their use in wastewater treatment

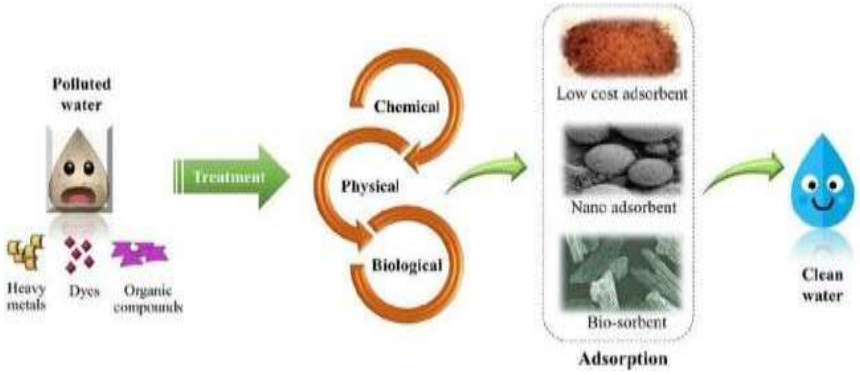

Fig.2. Phase-Changing Technologies

(Source: https://link.springer.com/article/10.1007/s11356-021-12395-x**)**

3. MATERIALS AND METHODS

3.0. Materials:

Apparatus utilized for the experimental approach:

- Wrist Action Shaker
- UV visible spectrophotometer
- Cuvettes
- Conical Flasks
- Beakers
- Measuring Jars
- Weighing Balance

Reagents utilized for conducting the experimental approach:

- Methylene blue (Solute or Adsorbate)
- Ulva lactuca (Adsorbent)

3.1. Methods:

3.1.1. Experimental methods:

3.1.1.1. Adsorbent preparation:

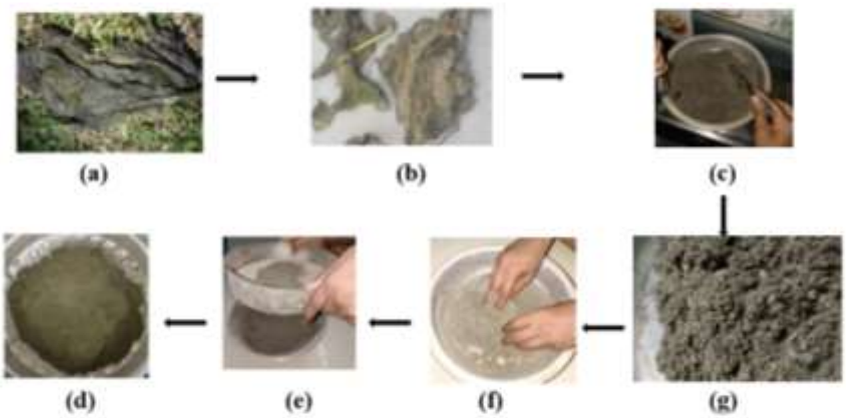

Fig. 3. Adsorbent preparation.

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- 1 kg of Algae were collected from sea shores of Visakhapatnam.
- The algae were washed with distilled water and dried under sun for 48hrs.
- After drying the weight was reduced to 400g. the dried algae was crushed to fine particles
- Sieving was done through different mesh no. they are - 200, -150, -100B.S.S.
- At last, we stored the adsorbent (algae powder) according to their size.

3.1.1.2. Sample Preparation:

For preparation of one per gram of adsorbent for different initial concentrations of the solution with constant amount of dosage of adsorbent. Algae bio-mass powder quantity is kept constant (Size of the adsorbent chosen is -200B.S.S.). The initial concentration of the solution is maintained at 2,4,6,8,10 PPM are tested. Sample used for scheme experimental approach.

Fig. 4. Methylene blue

Table:1. ***Sample Preparation***

S.No	Quantity of solute (Methylene Blue)(mg)	Quantity of distilled water (liters)	Acquired concentration Of the colored solutionm(mg/lit or ppm)
1	2	1	2
2	4	1	4
3	6	1	6
4	8	1	8
5	10	1	10

Concentration of the solution = Quantity of Methylene Blue (mg) / Quantity ofdistilled water(liter)

= 2mg/1 litre = 2ppm

3.1.2. Analytical method:

3.1.2.1. Effect of initial concentration:

To determine the removal of solute per gram of adsorbent when initial concentration of the colored solution (Methylene Blue solution) is changed. The quantity of adsorbent (Algae powder) is taken as 1gm. The size of adsorbent chosen is -200B.S.S. The initial concentration of the solution is maintained at 2ppm, 4 ppm, 6 ppm, 8 ppm and 10ppm are tested.

Procedure:

- Solution sample of 5nos with different initial concentrations were prepared.
- For conducting the UV Visible spectrophotometry, a reference sample was tested with 665 nm wavelength.
- Initial absorbance is noted through UV Visible spectrophotometer by taking the sample in a well cleaned cuvette.
- To the solution samples of different initial concentrations, add 1gm of adsorbent (algae powder).
- Weight of adsorbent is measured through weighing balance.

- Conical flasks are fixed to wrist action shaker holder with required stiffness.
- Ensuring that the requirements to start the process are fulfilled, and then the process is started.
- After starting the process, the wrist action shaker is to be left for 30mins at a speed of 5 points.
- After 30mins, wrist action shaker is stopped and sample is filtered through filter paper in measuring jar.
- Final absorbance of colored solutions is determined after adsorption by using uv visible spectrophotometer by taking the sample in a well cleaned cuvette.
- The concentration of the colored solution after adsorption is calculated. Adsorption efficiency is also calculated. Removal of solute per gram of adsorbent is calculated.

C_{Final} $=C_{Inital}[A_{Final}/A_{Intia}l]$

$=10[0.116/1.458]$

$=0.32$

Removal of solute per gram of adsorbent $=[[C_{Intial}-C_{Final}]*Volume]/Dosage\ of\ adsorbent$

$=[[10-0.76]*0.1]/1$

$=9.24$

Adsorption efficiency $=[[C_{Intial}-C_{Final}]/C_{Intial}]*100$ $=[[10-0.76]/10]*100$

$=92.4\%$

3.1.2.2. Effect of adsorbent dosage:

To determine the removal of solute per gram of adsorbent when initial concentration of the colored solution (Methylene Blue solution) is constant at 10ppm and different quantity of adsorbent is taken. The size of adsorbent chosen is -200B.S.S. The quantities of adsorbent taken are 1gm, 2gm, 3gm and 4gm.

Procedure:

- Solution sample of 5nos with constant initial concentrations were prepared.
- For conducting the UV Visible spectrophotometry, a reference sample was tested with 665 nm wavelength.
- Initial absorbance is noted through UV Visible spectrophotometer by taking the sample in a well cleaned cuvette.
- The solution of known concentration is then taken in 4nos conical flasks in order to add different quantity of adsorbent (algae powder)
- Weight of adsorbent is measured through weighing balance.
- Conical flasks are fixed to wrist action shaker holder with required stiffness.
- Ensuring that the requirements to start the process are fulfilled, and then the process is started.
- After starting the process, the wrist action shaker is to be left for 30mins at a speed of 5 points.
- After 30mins, wrist action shaker is stopped and sample is filtered through filter paper in measuring jar.
- Final absorbance of colored solutions is determined after adsorption by using uv visible spectrophotometer by taking the sample in a well cleaned cuvette.
- The concentration of the colored solution after adsorption is calculated. Adsorption efficiency is also calculated. Removal of solute per gram of adsorbent is calculated.

C_{Final} $=C_{Inital}[A_{Final}/A_{Intia}l]$

$=10[0.071/1.588]$

$=0.45$

Removal of solute per gram of adsorbent $=[[C_{Intial}-C_{Final}]*Volume]/Dosage\ of\ adsorbent$

$=[[10-0.45]*0.1]/1$

$=9.55$

Adsorption efficiency =[[C_{Intial}-C_{Final}]/C_{Intial}]*100

=[[10-0.45]/10]*100

=95.5%

3.1.2.3. Effect of pH:

To determine the removal of solute per gram of adsorbent when initial concentration of the colored solution (Methylene Blue solution) is constant. The quantity of adsorbent (Algae powder) is taken as 1gm. The size of adsorbent chosen is -200B.S.S. The initial concentration of the solution is maintained at constant 10(ppm) and pH varies 2pH, 4pH, 7pH, 11pH.

Procedure:

- Solution sample of 4nos with constant initial concentrations were prepared.
- For conducting the UV Visible spectrophotometry, a reference sample was tested with 665 nm wavelength.
- Initial absorbance is noted through UV Visible spectrophotometer by taking the sample in a well cleaned cuvette.
- To the solution samples of different initial concentrations, add 1gm of adsorbent (algae powder).
- Weight of adsorbent is measured through weighing balance.
- Conical flasks are fixed to wrist action shaker holder with required stiffness.
- Ensuring that the requirements to start the process are fulfilled, and then the process is started.
- After starting the process, the wrist action shaker is to be left for 30mins at a speed of 5 points.
- After 30mins, wrist action shaker is stopped and sample is filtered through filter paper in measuring jar.
- Final absorbance of colored solutions is determined after adsorption by using uv visible spectrophotometer by taking the sample in a well cleaned cuvette.
- The concentration of the colored solution after adsorption is calculated. Adsorption efficiency is also calculated. Removal of solute per gram of adsorbent is calculated.

C_{Final} =C_{Inital}[A_{Final}/A_{Intia}l]

=10[0.116/1.458]

=0.32

Removal of solute per gram of adsorbent =[[C_{Intial}-C_{Final}]*Volume]/Dosage of adsorbent

=[[10-0.76]*0.1]/1

=9.24

Adsorption efficiency =[[C_{Intial}-C_{Final}]/C_{Intial}]*100

=[[10-0.76]/10]*100

=92.4%

4. RESULTS & DISCUSSION

4.0. Result

4.1. Effect of Initial Concentration:

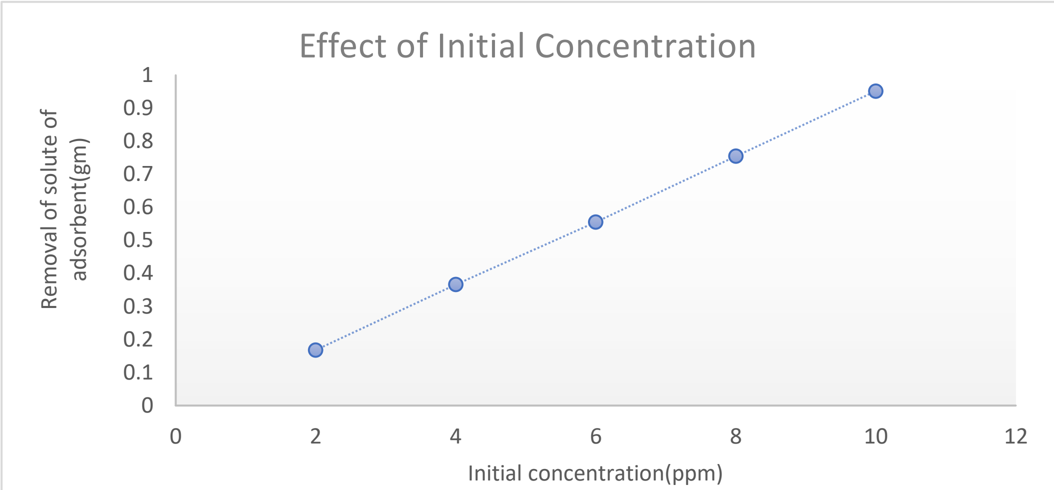

Fig. 5. Graphical representation for the effect of initial concentration

Table 2. Effect of initial concentration

S.No	Dosage of adsorbent (gm)	$A_{Initial}$	Initial Concentration (PPM)	A_{Final}	Final Concentration (PPM)	Removal of solute per gram of adsorbent*[10^{-4}]	Adsorption Efficiency(%)
1	1	0.441	2	0.071	0.32	1.68	84
2	1	0.813	4	0.070	0.34	3.66	91.5
3	1	0.948	6	0.071	0.449	5.551	92.5
4	1	1.268	8	0.071	0.447	7.553	94.5
5	1	1.558	10	0.075	0.48	9.52	95.2

Due to decrease in initial concentration there occurs decrease in driving force for the solute transfer there occurs decrease in driving force for the transfer of color ingredient to the adsorbent surface. Hence there occurs there occurs decrease in removal of solute per gram of adsorbent.

4.2. Effect of Dosage of Adsorbent

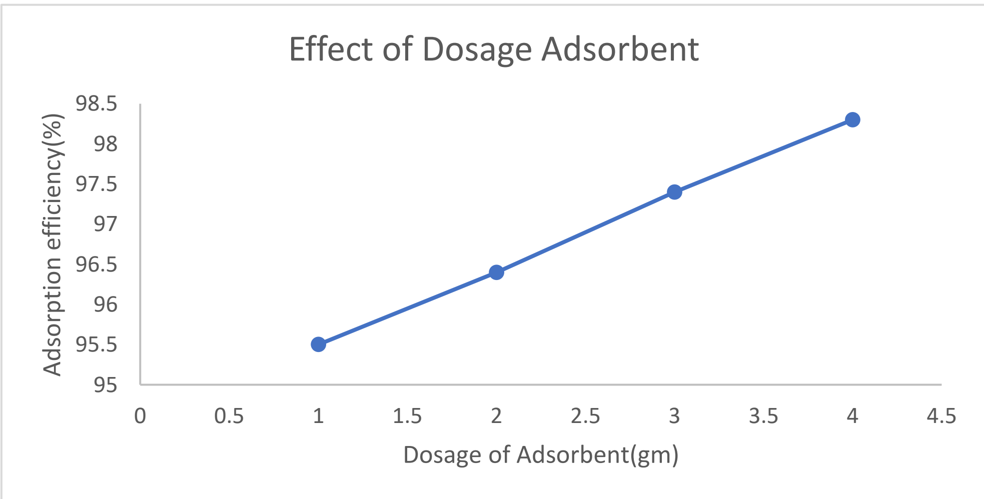

Fig. 6. Graphical representation for the effect of adsorbent dosage

Table 3. Effect of adsorbent dosage

S.No.	Dosage of adsorbent (gm)	$A_{Initial}$	Initial Concentration (PPM)	A_{Final}	Final Concentration (PPM)	Removal of solute per gram of adsorbent*[10^{-4}]	Adsorption efficiency
1	1	1.588	10	0.071	0.45	9.55	95.5
2	2	1.588	10	0.057	0.36	4.82	96.4
3	3	1.588	10	0.041	0.26	3.247	97.4
4	4	1.588	10	0.027	0.17	2.4575	98.3

Due to increase in the dosage of the adsorbent in the solution, there occurs an increase in concentration difference. Hence the driving force necessary for solute transfer increases. Due to which, there is an increase in adsorption efficiency.

4.3. Effect of pH:

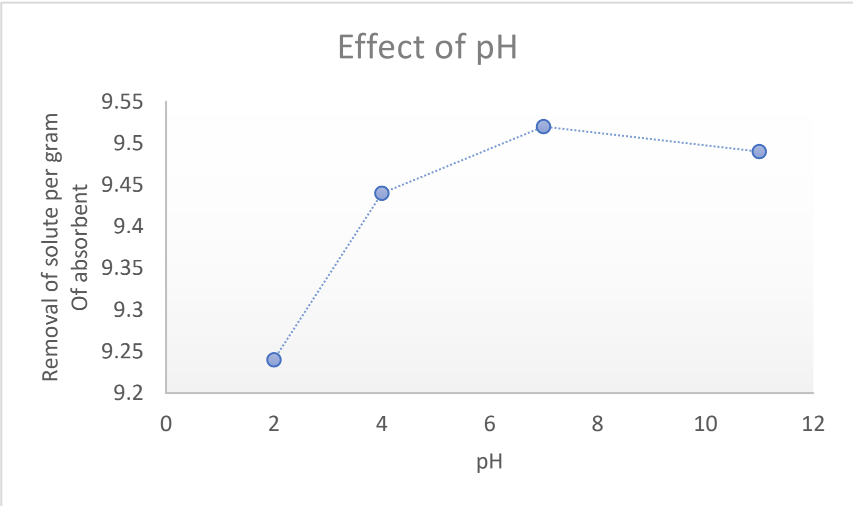

Fig. 7. Graphical representation for the effect of pH

Table 4. Effect of pH

S.No.	Dosage of adsorbent (gm)	pH	$A_{Initial}$	Initial Concentration (PPM)	A_{Final}	Final Concentration (PPM)	Removal of solute per gram of adsorbent*[10^{-4}]	Adsorption Efficiency (%)
1	1	2	1.458	10	0.116	0.76	9.24	92.4
2	1	4	1.679	10	0.095	0.56	9.44	94.4
3	1	7	1.588	10	0.075	0.48	9.52	95.2
4	1	11	1.549	10	0.080	0.51	9.49	94.9

At pH 7, there is an increase in adsorption efficiency. But at other pH the adsorption efficiency is relatively low.

5.0. Conclusion

By conducting experiment for effect of initial concentration, where the quantity of adsorbent is kept constant and the initial concentration of the colored solution is varying, it can be concluded that, with a decrease in the initial concentration of the colored solution, there is a decrease in the removal of solute per gram of adsorbent.

By conducting experiment for effect of dosage of adsorbent, where the concentration of the colored solution is kept constant and the quantity of adsorbent is varied, it can be concluded that, with an increase in adsorbent quantity there is an increase in the adsorption efficiency.

By conducting experiment for effect of pH, where the concentration of the colored solution and the quantity of adsorbent are kept constant and the pH varied, it can be concluded that, at pH 7, there is an increase in adsorption efficiency. But at other pH the adsorption efficiency is relatively low.

5.1. Future scope of work:

Study of adsorption isotherms is to be conducted and characterization of the adsorbent is to be done.

Further investigation and comparison with other adsorbents have been done. Effect of temperature is to be tested.

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