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Bio Sorption of Acid Violet 4BS from Aqueous Solution and Textile Industry Wastewater Using *Syzygium Cumini* Seeds

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Abstract: **Application of *Syzygium cumini* seeds as bio sorbent for the removal of Acid Violet 4BS dye from aqueous solution and textile industry wastewater was investigated. Batch experiments were carried out to determine the effect of pH, particle size, bio sorbent dose, contact time and initial dye concentration. Characterization of bio sorbent was also done by SEM and FTIR. Maximum dye bio sorption of 91.20% was achieved at pH 2.0, particle size 212µm, bio sorbent dose of 1g/L, contact time of 60mins and initial concentration of 50mg/L. The equilibrium bio sorption data fitted well to Langmuir than Freundlich isotherm models with Langmuir monolayer bio sorption capacity of 20.0 mg/g and Freundlich bio sorption capacity of 11.78 (mg/g) (mg/L) $^{1/n}$. The bio sorption results in this study indicated that *Syzygium cumini* seeds are attractive option for removing acidic dyes from the wastewater**

Keywords: **Acid Violet 4BS; Bio sorption; Isotherm; *Syzygium cumini* seeds.**

I. INTRODUCTION

Dyes are the toxic and trace material available in the waste water. Dyes usually have a complex aromatic molecular structure which makes them more stable and difficult to biodegrade [1] .Dyes are basically chemical compounds that can attach themselves to fabrics or surfaces to impart colour. Most dyes are complex organic molecules and are resistant to weather, action of detergents, etc. Synthetic dyes are extensively used in many fields of up-to-date technology, e.g., in various branches of the textile industries, leather industries, paper production, food industries, hair colouring industries and so on [2],[3]. Even at low concentration (1 ppm), dyes could be highly noticeable, and could cause an aesthetic pollution and disturbance to the ecosystem and water sources [4]The adverse effect of these dyes has not only been seen on the environment and also a major concern regarding human health. It has not only polluted the nature by slowly increasing the biomagnifications of the chemicals regarding in imbalance of hormones and immunity loss even results in cancer [5].

Synthetic dyes are used in various industries for various purposes and they removal from the effluent has now been an issue of concern as a result series of methods are followed for the removal of dyes. There are various conventional methods such as chemical coagulation using alum, lime, ferric sulphate [6], oxidation methods using chlorine and ozone [7] biological treatments, floatation[8] and many more which has a draw back as it is expensive, inefficiency and sludge disposal problem[9] Hence the industries interest and main approach is towards low cost and effective method which can remove the dyes from the effluent or wastewater and support in maintaining the balance of nature, hence the approach of processes like adsorption or biosorption using agricultural or low cost material is been favourable by the industries. Recently, biosorption has been recommended as cheaper and more effective technique for dye contaminated wastewater treatment [10]

The present study investigates the bio sorption of Acid Violet 4BS (AV4BS) dye from aqueous solution and textile industrial wastewater using *Syzygium cumini* seeds (SCS). The effect of pH, particle size, bio sorbent dose, contact time and initial dye concentration on bio sorption were studied in detail. Langmuir and Freundlich isotherm models were used to fit the equilibrium data

II. MATERIAL AND METHODS

The Acid Violet 4BS (AV4BS) dye was obtained from Zese India LTD, Bangalore, Karnataka. Its IUPAC name is 3-[(4-Amino-phenyl)-hydrazono]-5-hydroxy-4-oxo-3, 4-dihydro-naphthalene-2, 7-disulfonic acid. The molecular formula is $C_{16}H_{13}N_3NaO_8S_2$, molecular weight is462.42 [g/mol] and structure of the AV4BS is shown in figure 1.

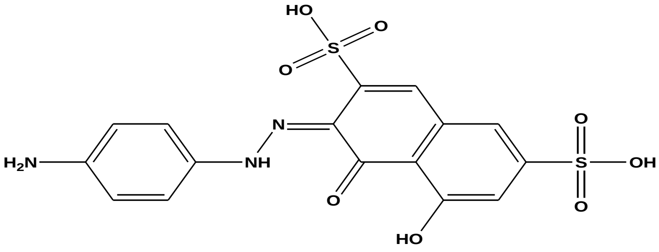

Fig 1- Structure of AV4BS

2.1 Dye solution preparation:

An accurately weighed quantity of acid AV4BS dye was dissolved in double distilled water to prepare stock solution (1000mg/L) and further diluted to obtain working solutions of lower concentration which was determined using the absorbance values before and after the bio sorption using UV-Vis Spectrometer(HitachiUV-2910). The pH adjustment of solution was carried out using 0.01N HCl and 0.01N NaOH.

2.2 Preparation of bio sorbent:

The plant *Syzygium cumini* belongs to the family Myrtaceae. *Syzygium cumini*, is also called as jambul, jambolan, jamblang, or jamun, which is an evergreen tropical tree in the flowering plant . The seeds of *Syzygium cumini* (SCS) are used in this study. The seeds were collected, washed thoroughly and dried it in the sunlight. Subsequently the seeds were grounded and sieved. Biosorbent was washed thoroughly and constantly several times using double distilled water and dried well in the sunlight. SCS stored in a dried and an airtight container for experimentation work.

2.3 Characterization of bio sorbent:

The scanning electron microscope of SCS was carried out by ZEISS, (EVO/LS-15-15-41, Smart SEM version 5.05). The FTIR analyses were carried out by Shimadzu FTIR spectrophotometer.

2.4 Batch experiments:

Batch experiments were carried out at room temperature. For experimental run 100ml of stock solution containing 50mg/L of SCS at required pH level were taken in 250ml Erlenmeyer flasks. Known amount of SCS was added and the mixture was shaken at 170rpm using mechanical shaker (KEMI KRS 110, India) for a fixed period of time. The stock solution mixture was then filtered from SCS and determined spectrophotometrically by recording the absorbance changes at maximum adsorption (600nm) using UV-Vis Spectrometer (HitachiUV-2910). All determinations were done in triplicate average values were considered. Percentage adsorption was calculated by the formula

$$\%Biosorption = \left(\frac{C_i - C_f}{C_i}\right) \times 100 \qquad (1)$$

Where C_i and C_f are the initial and final AV4BS concentration (mg/L) respectively.

2.5 Effect of pH:

In 250ml Erlenmeyer flasks a range of 100ml of stock solution containing 50mg/L of AV4BS was taken. To this 1g/L of 212 µm particle size of SCS were added to each and the determinations were done by the usage of 0.01N HCl and 0.01N NaOH respectively to obtain various range of pH from 1.0 to 10.0. After 60min of shaking, the solution was filtered and determined spectrophotometrically.

2.6 Effect of particle size:

The particle size variation was carried out according to the ASTM standards (American Society Testing Materials) where the size ranges from 212µm, 250µm, 355µm, to 500µm. Hence 50mg/L of AV4BS was taken in 250ml of Erlenmeyer flasks, of SCS with (1g/L) with pH level 2.0 and agitated for 60mins. The supernatant was then observed spectrophotometrically.

2.7 Effect of Bio sorbent Dose:

SCS of 212µm at varying of 0.1 to 2.0g/L were taken separately in 250ml Erlenmeyer flasks to that 100 ml of stock solution of AV4BS of 50mg/L was added and the pH level was adjusted to 2.0 and that mixture was kept for shaking for a period of 60min in mechanical shaker and later filtered and determined spectrophotometrically.

2.8 Effect of Contact Time:

100ml of stock solution (containing AV4BS of 50mg/L) was taken in 250ml of Erlenmeyer flasks. The pH was fixed to 2.0 and SCS of 212µm at 1g/L was added to each. The mixture of SCS and AV4BS solution was shaken in the mechanical shaker for the time interval of 10, 20, 30, 40, 50, 60, to 120mins respectively. The residual concentration of the mixture of each was filtered and determined by spectrophotometer.

2.9 Effect of initial dye concentration:

Various concentrations of 10, 20, 30, 40, 50mg/L of stock solution of 100ml were taken in 250ml Erlenmeyer flasks. Particle size 212µm of SCS (1g/L) was added to each which had been adjusted with the pH level of 2.0. That associate solution was agitated for a period of 60min in mechanical shaker. The absorbed AV4BS was then filtered and determined by spectrophotometer

2.10 Physico-chemical characteristics of textile industry wastewater:

The wastewater was collected from textile industry located in Bangalore, Karnataka India. The physico-chemical characteristics were determined using standard method [11]. The characteristics of physico-chemical characteristics are presented in Table 1.

TABLE 1: PHYSICO-CHEMICAL CHARACTERISTICS OF TEXTILE INDUSTRY WASTEWATER

Characteristics	Contents(mg/L)
Colour	Light violet
pH	9.13
EC(µs/cm)	2108
TDS	894
Total hardness	657.8
Calcium	185.6
Magnesium	96.5
Chloride	470.7
Sulphate	301.4
DO	Nil
BOD	1154.1
COD	1599.2

III. RESULTS AND DISCUSSION

3.1 Scanning Electronic Microscopic Studies (SEM):

SEM is widely used to study the morphology features and surface characteristics of the bio sorbent. It also reveals the surface texture and porosity of bio sorbent. Figure 2a and 2b shows that the surface of the bio sorbent SCS before and after bio sorption, where SCS becomes wider due to bio sorption of AV4BS.the comparison of both the figures describes the porosity clearly, where the pore size of the particle has increased. It also plays an important role in determining the surface availability for the bio sorption of AV4BS on SCS.

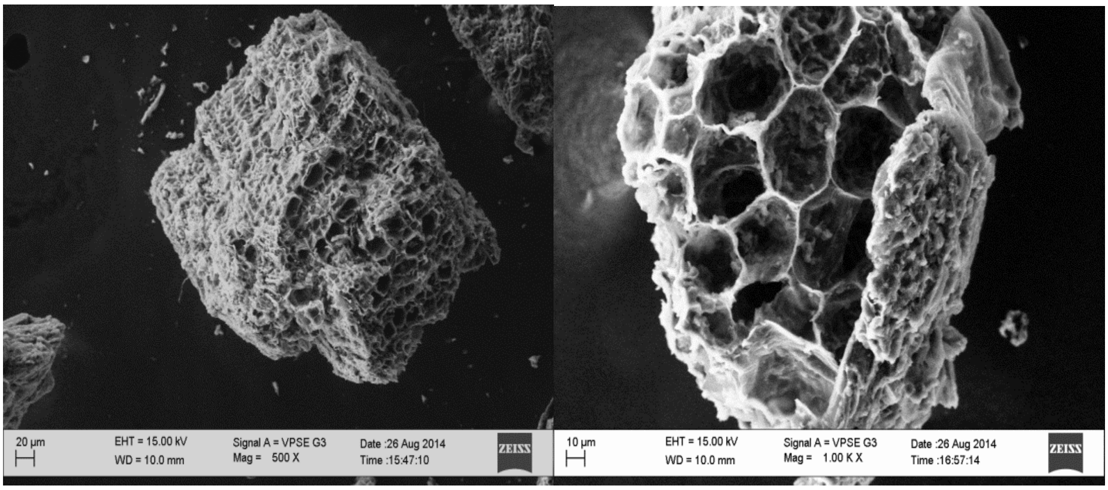

Fig 2a- SCS before biosorption of AV4BS b- SCS after biosorption of AV4BS

3.2 FTIR Analysis:

The spectra were measured in the wave number range of 400-4000cm^{-1}. Figure 2a and 2b shows the FTIR spectra of AV4BS before biosorption on SCS and AV4BS after biosorption on SCS. The bands show the functional groups of sulphur and carboxylic acid and their derivatives. Some peaks are shifted or disappeared, some new peaks have been determined. These changes in the peaks definitely indicate the functional groups on the surface of the SCS in biosorption process. Peak ranging from 544.753cm^{-1} is due to S-S bonds in figure 2a which reduced in the figure 2b as observed; this is due to the biosorption of AV4BS on SCS. The peaks between 1539 and above 3300 cm^{-1} indicates N-H bonds and C-N bonds of amine along with overlap C-H stretched bands. The peaks which are reduced in figure2b indicate strong stretching vibration of carboxylic acids groups of amide. An FTIR spectrum of fig 2b shows peaks in low frequency regions because there is a biosorption of AV4BS on SCS surface. Decreased intensity of sharp peaks concluded that AV4BS has been functionalized by SCS.

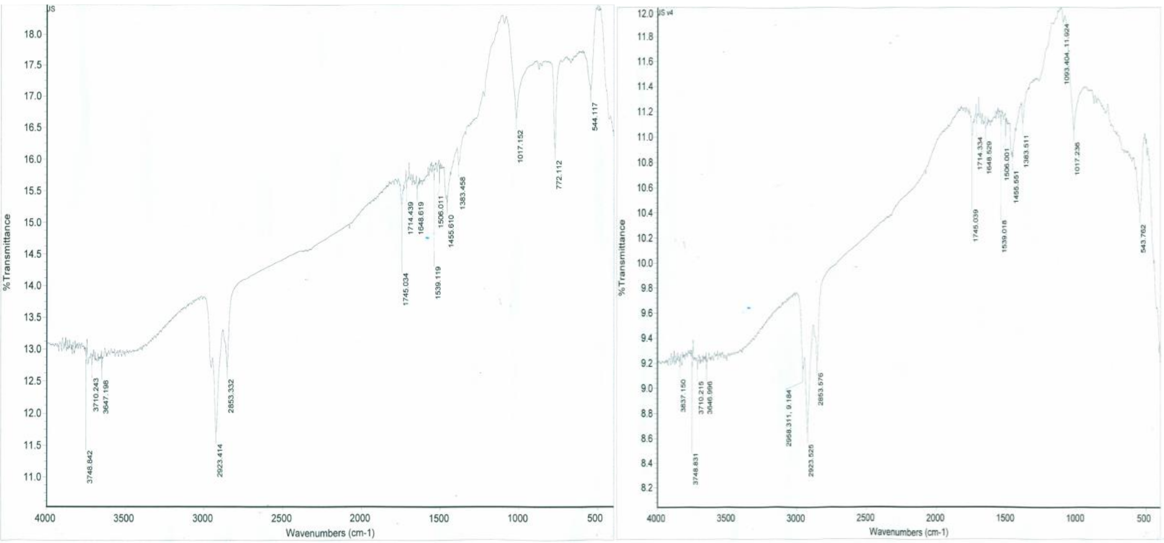

Fig-3 a. FTIR of SCS before biosorption of AV4BS b FTIR of SCS after biosorption of AV4BS

3.3 Effect of pH:

The pH of the dye solution has a great influence on the biosorption of the dye on the biosorbent as it effect on the surface properties of the biosorbent, ionization or dissociation of the dye molecules[12], [13] .Figure 4 shows the effect of pH on the removal of AV4BS. The highest dye removal efficiency was observed at pH 2.0. The removal percentage then decreased as pH increased from 3 to 10. This is due to the H_3O^+ ions which were replaced by OH^- ions as the pH increases it makes the surface negatively charged, similar results were recorded in the other acidic dyes in the process of biosorption. [12], [13], [14].

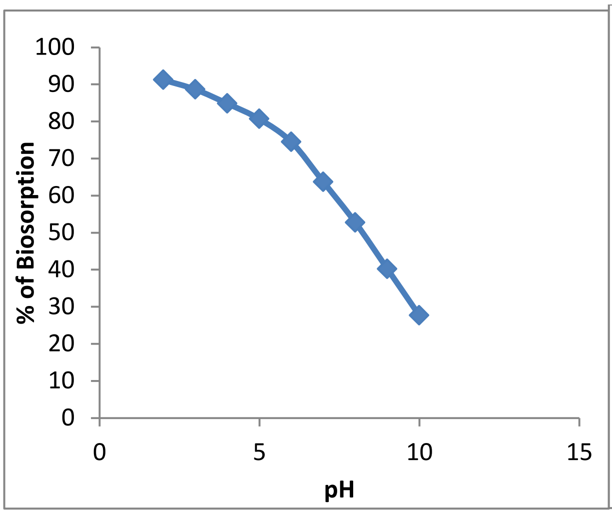

Fig-4 Effect of pH on biosorption of AV4BS by SCS

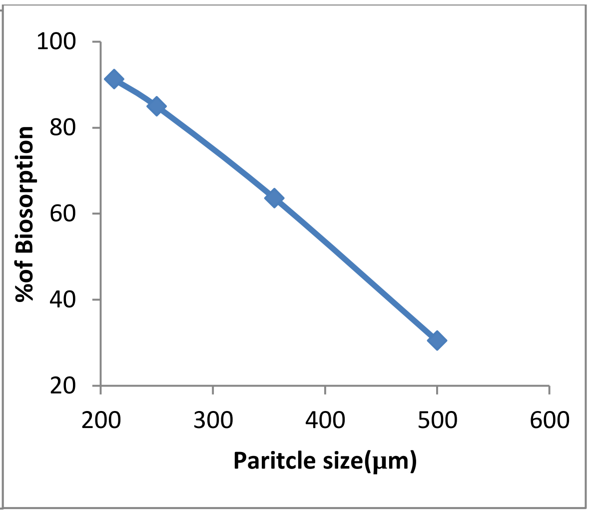

Fig-5 Effect of particle size on biosorption of AV4BS by SCS

3.4 Effect of Biosorbent Particle size:

The effects of particle size on the biosorption of the AV4BS on to SCS are shown in the figure 5. The results describes that the percentage removal of the AV4BS increases with decrease in SCS particle size which was achieved at 212µm. This clearly described that decrease in the particle size would increase in the surface area and consequently an increase in AV4BS biosorption onto the SCS surface occurs. Various factors are responsible for the low biosorption capacity of the AV4BS on the biosorbent large particles. [1], [15], [16].

3.5. Effect of Biosorbent Dose:

The biosrbent doses on AV4BS by SCS are shown in figure 6. The results describes that AV4BS biosorption by SCS increases with increasing in the biosorbent dose from 0.2 to 2g/L (28.30 to 91.20%).This is due to the increase in surface area which in turn increases the availability of the exchangeable sites on the SCS for the biosorption of AV4BS.[17]. Further increase in biosorbent dose beyond 1g/L keeps AV4BS biosorption static which suggest that it has attained equilibrium between the liquid and solid phase. Similar results were observed by [18], [19].

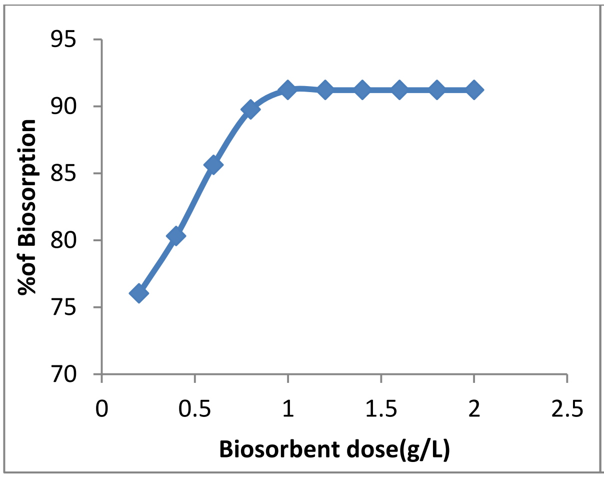

Fig-6 Effect of Biosorbent dose on biosorption of AV4BS by SCS

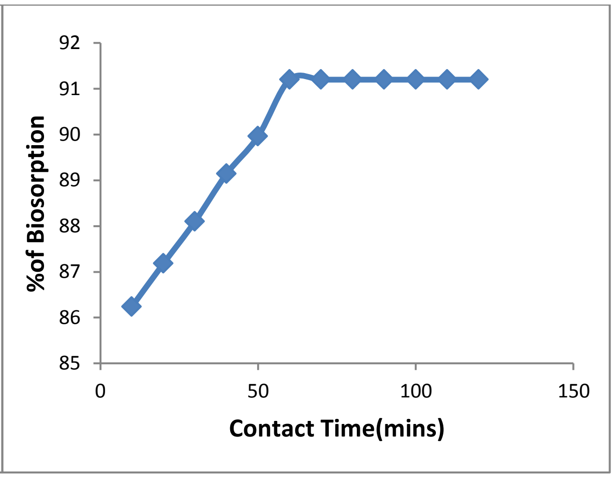

Fig-7 Effect of contact time on biosorption of AV4BS by SCS

3.6 Effect of Contact time:

The variation of contact time of AV4BS by SCS is shown in figure 7. It was clear that maximum biosorption (91.20%) of AV4BS by SCS was achieved at 60min. A rapid biosorption of the AV4BS by SCS took place at 30min and than the biosorption was slow till it reached the equilibrium. The reason being that, at initial stage there was a more vacant biosorption site which gets occupied later resulting in the slow biosorption and once the biosorption reaches the equilibrium the contact time and percentage of biosorption becomes constant.[20],[21],[22].

3.7 Effect of initial dye concentration:

Figure 8 shows the initial concentration of AV4BS by SCS which describes that the percentage of biosorption decreases (99.60% to 91.20%) with increase in the concentration. This is due to the fact that in dye ion concentration causes saturation of biosorption sites on SCS and this blocks further AV4BS biosorpted on biosorption sites as a result the biosorption efficiency decreases. [19], [23], [24].

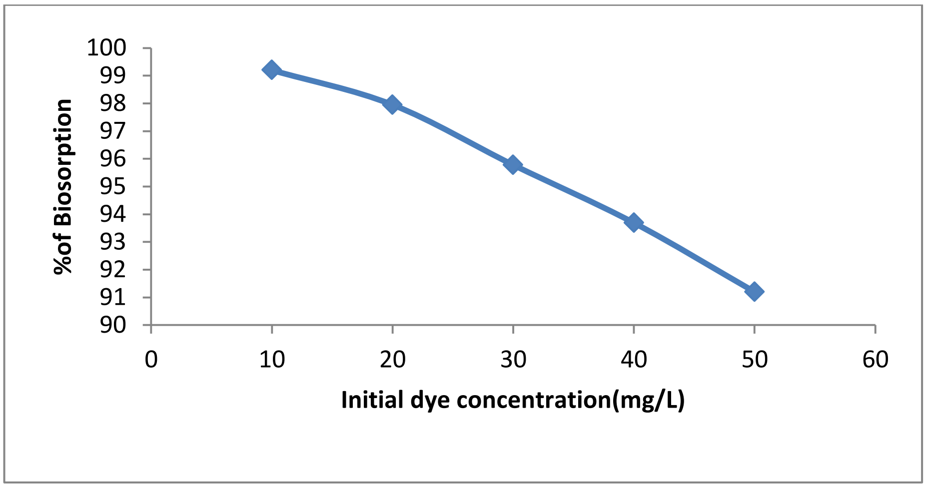

Fig-8 Effect of Initial dye concentration on biosorption of AV4BS by SCS

3.8a Langmuir isotherm:

Langmuir isotherm model was applied to describe the biosorption ofAV4BS. The Langmuir isotherm [25] model is represented by the following equation.

$$\frac{C_e}{q_e} = \frac{1}{(bq_{max})} + \frac{C_e}{q_{max}} \qquad (2)$$

Where, C_e is the equilibrium concentration (mg/L), q_e and q_{max} are the equilibrium and maximum biosorption capacity (mg/g), respectively and b is the equilibrium constant.

Figure 9 shows the linear plot obtained by plotting C_e/q_e versus C_e. The Langmuir model parameters Q_{max} (mg/g) and b (L/g) statistically fits the biosorption data which are presented in Table 2. The Langmuir model effectively describes the biosorption data R^2 value of 0.981. This behaviour indicates a monolayer biosorption. The values of b (0.0499 L/g) and Q_{max} (20.0mg/g) indicates maximum interaction and greater affinity of AV4BS with SCS [23].

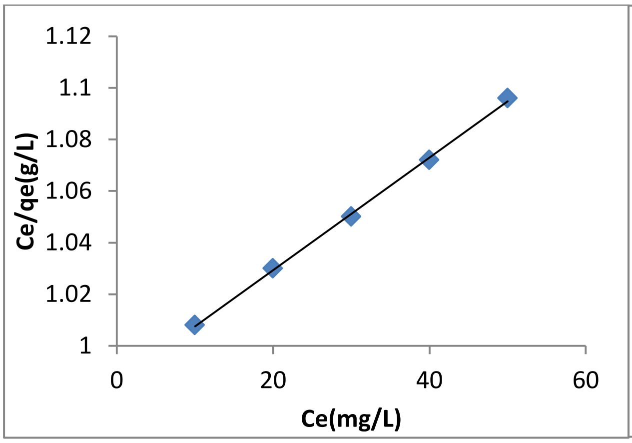

Fig: 9 Linear form of the Langmuir isotherm for AV4BS by SCS.

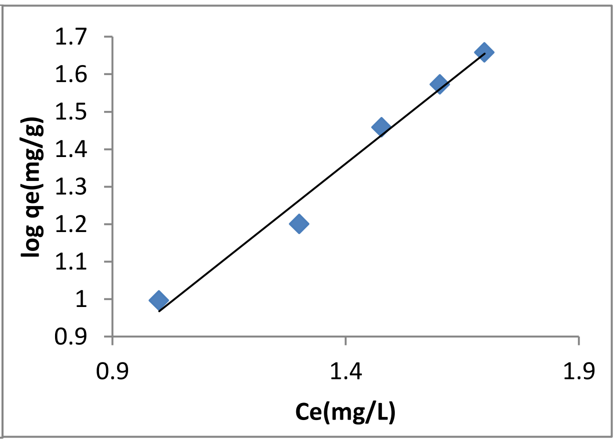

Fig: 10 Linear form of the Freundlich isotherm for AV4BS by SCS

3.8b Freundlich isotherm:

Freundlich isotherm model is also applied to describe the adsorption of AV4BS. Linearized in logarithmic form of Freundlich isotherm [28] model equation is represented by.

$$log q_{e=} log K_f + \left(\frac{1}{n}\right) log C_e \quad (3)$$

Where K_F and n are the Freundlich constant and '1/n' is the heterogeneity factor.

Figure 10 shows the linear plot obtained by plotting log q_e versus log C_e. The Freundlich model parameters like R^2 values, K_f (mg/g) (mg/L) $^{1/n}$ and n are given in Table 2. The results indicate that biosorption data for AV4BS fits well to Langmuir model than Fruendlich model. Hence biosorption was monolayer coverage of AV4BS on SCS and the homogeneity of binding sites on biosorbent surface [29], [30]. Table 3 describes the comparison of Q_{max} values of other work along the present study.

TABLE -2 LANGMUIR ISOTHERMS AND FREUNDLICH ISOTHERM PARAMETERS FOR BIOSORPTION BY SCS

Dye	Langmuir isotherm			Freundlich isotherm		
AV4BS	Q_{max} (mg/g)	b(L/g)	R^2	K_f(mg/g)(mg/L)$^{1/n}$	n	R^2
	20.0	0.0499	0.998	11.78	0.933	0.981

TABLE -3: COMPARISON OF SORPTION CAPACITY OF VARIOUS SEEDS AS BIOSORBENTS

Dye	Biosorbent	Sorption capacity	References
Acid Blue 324	mango seed	12.8	[31]
Acid Green 25		8.6	
Acid Orange 7		17.3	
Acid Red 1		11.2	
Reactive Black 5	sunflower seed shells	0.873	[32]
Acid Violet4BS	*Syzygium cumini* seeds	20.0	Present study

3.9 Application of Textile industry wastewater

The efficiency of SCS for AV4BS from textile industrial wastewater was determined. The experiment was performed in an Erlenmeyer flask containing 50ml of waste water sample. To this 212µm of 1g/L of SCS was added and pH was adjusted to 2.0 using 0.01N HCl and 0.01N NaOH. After 60min of agitation, the wastewater sample was filtered and the resultant supernatant solution was analysed by U.V.spectrophotometer (HitachiUV-2910). The result described that AV4BS biosorption from textile industrial wastewater was 86.22% which was less than the aqueous solution. This is due to competition between ions of dyes and co-ions interference for the biosorption sites on the SCS.

IV. CONCLUSION

The present study investigated the biosorption of AV4BS by SCS from aqueous media and textile industry wastewater. Characterization of biosorbent shows clearly the porosity and wider surface texture and the FTIR peaks also revealed that biosorption occurred. The biosorption equilibrium was described by the isotherm model. A single-stage batch biosorption system was design for the AV4BS removal which was also outlined based on the isotherm model. Langmuir model data fits well than Fruendlich model, proving biosorption was monolayer coverage of AV4BS on SCS. And when the SCS was applied for textile industry wastewater, percentage of biosorption was less compare aqueous solution as the competition between ions of dyes and co ions interaction. It was concluded that the SCS could be used as a promising alternative for AV4BS removal from aqueous solutions and textile industry wastewater.

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