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ADSORPTION STUDIES ON REACTIVE YELLOW-14 DYE USING THE LEAVES OF *Averrhoa bilimbi*

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ABSTRACT
The adsorbent prepared from *Averrhoa bilimbi* was used to remove Reactive Yellow-14 dye from wastewater by adsorption. Various parameters like Biomass dose, Equilibration time, pH were studied. The adsorption isotherms have been analyzed and fitted with the Freundlich model. Kinetic studies fit pseudo first order equation. It was concluded that the dye, Reactive Yellow-14 interacts well with an eco-friendly biomass-based adsorbent, the dried leaf powder of *Averrhoa bilimbi.*
Keywords: Reactive Yellow Dye-14, *Averrhoa bilimbi*, Adsorption Isotherms, Kinetics

INTRODUCTION

Applications of Reactive dyes around the globe are mostly used as cellulose fibers that possess main properties, such as having different brilliant shades of colors, soluble in water, affordable cost, the formation of a chemical covalent bond with the hydroxyl group of cellulose fibers, anionic and the color of the dyes shows fastness to washing[1].Dyes are polymers, deeply colored and biodegradability is low in nature[2]. In spite of high solubility in water, that is well beyond to the naturally occurring chromophoric groups (like azo, oxazine group, anthraquinone, formazane, metallized azo and phthalocyanine) and the bridging groups (like ether or ester covalent chemical bond) linkages are present between dyes and fibers. Reactive dyes find applications in the wool, cellulose and nylon, individually or as fiber blend compounds[3].

Averrhoa bilimbi Linn. (Oxalidaceae, Common name: Bilimbi) is a common plant in Asia growing up to 15 m tall and 30 cm in diameter. Bilimbi is a nutritious fruit that grows mostly on the trunk of tall trees and it is a starchy fruit. Bilimbi is rich in Vitamin C. Not only vitamins and minerals the fruit also consists of ash, protein, moisture as well as fiber[4].Literature survey about this plant shows that *Averrhoa bilimbi* is mainly used as a folk medicine in the treatment of diabetes mellitus, hypertension, and as an antimicrobial agent[5]. There are many reports on various aspects of fruits of *Averrhoa bilimbi* such as pharmacognostic studies, antimicrobial activity, antipuritic, antipyretic, antihelmintheticproperties[6].

The bilimbi fruit was used in folk medicine to lower obesity in some southern parts of India. This gives an idea and led further studies on its antihyperlipidemic properties[7].

Bilimbi leaves 3-6 cm long, are alternate and cluster at branch extremities. There are around 11 to 37 alternate or sub-opposite oblong leaflets[8].In the Philippines, leaves are made into a paste and applied on skin eruptions, rheumatism, itches, mumps or swelling. They are also used for the bites of poisonous creatures.

Adsorption is a process where a solid is used for removing a soluble substance from the water and it is a cost-effective method for the removal of a pollutant from textile waste water due to the usage of low-cost adsorbent[9].Activated carbon adsorption is a highly promising method[10] for dye removal. But in the

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present study low-cost powdered dried leaves of *Averrhoa bilimbiis* used as an adsorbent to remove Reactive yellow-14 dye in aqueous solutions. Leaf biomass is a potential adsorbent for different dyes present in the wastewater of textile industries. Due to the porous structures of the leaves, they can adsorb dye molecules effectively[11].

EXPERIMENTAL

ABLP leaves were collected from Kochi, Kerala. It was cleansed extensively with water to remove mud and foreign particle, crushed into small pieces and dehydrated under sunlight until the wetness gets dry out. It is then sieved to 400 microns. The ABLP was cleaned by washing with double distilled water till the washings show no color and no turbidity. The cleaned ABLP was evaporated under the sunlight and kept in airtight containers.

Fig.-1: Leaves of *Averrhoa bilimbi*

Preparation of Stock Solution

Dye RY-14 is universally used in the fabric industry, pulp industry etc[1]. The dye is anionic. The chemical formula of RY-14 dye is $C_{20}H_{19}ClN_4Na_2O_{11}S_3$ and the molecular weight is 669 g/mol. 1 liter of distilled water was taken and 1gm of RY-14 was dissolved to prepare a bulk solution. The color of the solution was yellow. The experiment was performed by diluting the stock solution to our desired concentrations in 100 ml of distilled water.

Batch Experiment

Adsorbent dosage, equilibration period, the effect of pH on the adsorption of dyes on ABLP was investigated by the adsorption experiments. The experiment was carried in 250 ml stoppered reagent bottles with 100 ml dye solution in a shaker at 200 rpm. The dye solution of resulting concentration was determined using UV- visible spectrophotometer at the wavelength of maximum absorption at 375 nm respectively. The effect of pH was studied over a pH range of 2 to 10. 0.1N HCl and 0.1N NaOH were used to adjust the pH. The percentage (%) of dye removal was calculated using the equation:

$$\text{Percentage of Dye Removal (\%)} = (C_i - C_f)/C_i * 100 \quad (1)$$

Where,
C_i–Concentration of the Initial Dye
C_f -Concentration of the Final Dye

RESULTS AND DISCUSSION

Biomass Dosage

The adsorption of the dyes on raw material was studied by varying weight of the leaves of *Averrhoa bilimbi* biomass (0.1-1.9g/ml). The percentage of dye removal has been increased as the concentration of the adsorbent increases.

The maximum dye removal efficiency was observed at 1.9g biomass of *Averrhoa bilimbi* dose containing 100mg/L dye concentration.

Effect of Equilibration Period

Only a particular amount of adsorbate can be absorbed by an adsorbent. So the initial concentration is always important for an adsorbate solution. Amount of dye adsorbed versus time was plotted. The time variation plot indicates that the removal of dye has been increased with increase in time. At higher contact time, the rate of adsorption was found to be high. It was concluded a period of 240 minutes was necessary for the maximum percentage of dye removal by ABLP.

Table-1: Effect of Biomass Dose

S. No.	Weight of Biomass	% of dye removal
1	0.1	32.91
2	0.3	45.38
3	0.5	53.04
4	0.7	56.15
5	0.9	58.38
6	1.1	59.33
7	1.3	63.56
8	1.5	73.47
9	1.7	77.48
10	1.9	82.68

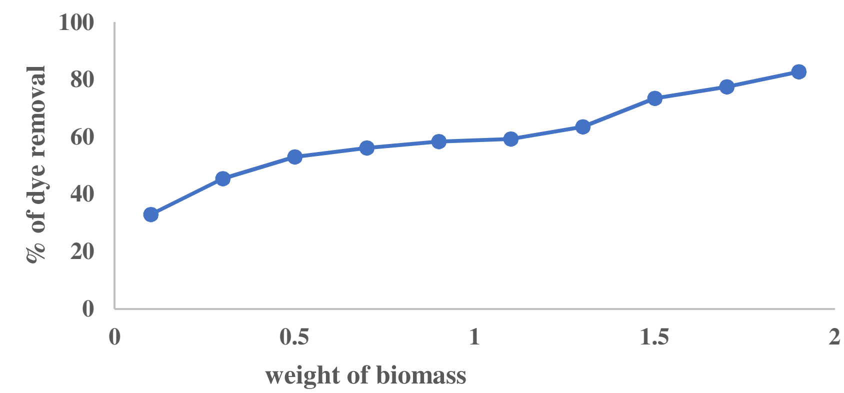

Fig.-2: Effect of Biomass on Biosorption of RY-14 Dye by the Biomass *Averrhoa bilimbi*

Table-2: Effect of Equilibration Period

S. No.	Time (min)	% of Dye Removal
1	10	44.56
2	20	48.19
3	30	51.42
4	60	54.98
5	90	61.91
6	120	65.58
7	150	72.64
8	180	76.92
9	210	80.16
10	240	84.19

Effect of pH

An important parameter in the adsorption process is pH. The pH of an aqueous phase has a greater influence on the upper layer of the adsorbent molecules. pH of the medium controls the extent of electrostatic charges provided by the molecules of dyes. The experiment was performed by taking different pH values from 2 to 10 and its adsorption capacity on ABLP was scrutinized. Figure-4 shows the change in pH on the RY-14 dye adsorption on ABLP.

The adsorption efficiency rapidly decreased as the pH of the dye solution increased. The Percentage removal of dye by ABLP was 80.64 % at solution pH of 2.Obtained results at optimum pH values of adsorbent were in good agreement with the values given in literature such as walnut shell, sawdust, clay, bentonite, native strains[12].

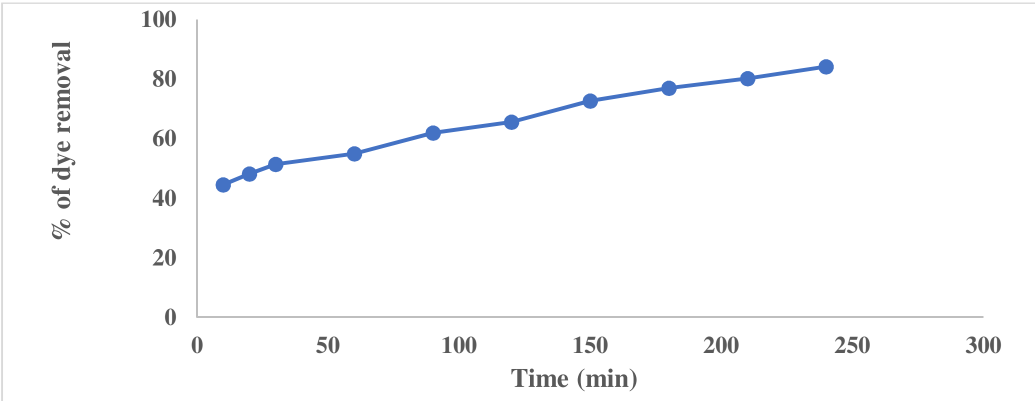

Fig.-3: Change in Equilibration Period on Sorption of Dye RY-14 by the Biomass *Averrhoa bilimbi*

At low pH, percentage of dye removal was high and this is due to the electrostatic interaction between the positive surface charge of the adsorbent and the anionic dye.
When the pH of the solution was high there is always electrostatic repulsion takes place between the molecules of dye and the positively charged surface, decreasing percentage of removal of anionic dyes and the capacity of adsorption.

Table-3: Effect of pH

S. No.	pH	% of Dye Removal
1	2	80.64
2	3	74.45
3	4	70.15
4	5	66.23
5	6	60.86
6	7	55.47
7	8	50.41
8	9	45.92
9	10	40.14

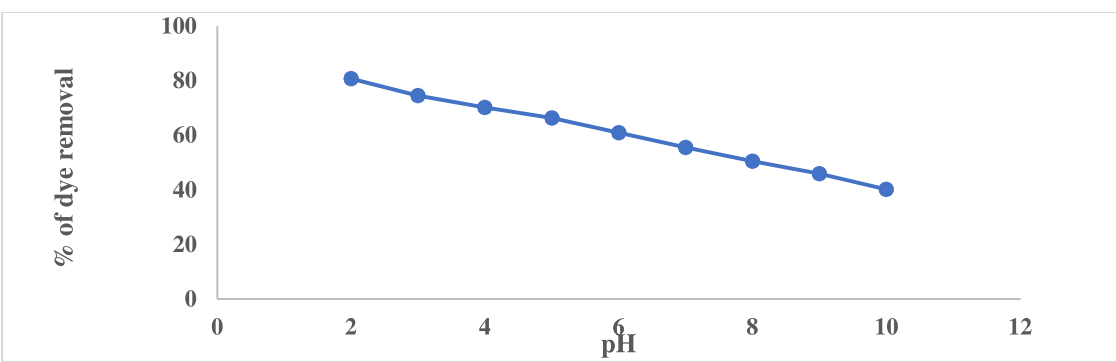

Fig.-4: Effect of pH of Dye RY-14 by the Biomass *Averrhoa bilimbi*

Adsorption Isotherm

The association between adsorbate and the adsorbent were well understood by the Isotherm studies[13]and this study is further extended to explain the removal of pollutants from aqueous solutions. In the current research, the adsorption of reactive yellow-14 on ABLP showed that the rate of removal of RY-14 increases with an increase in dye concentrations and attains saturation at higher concentrations[14]. Isotherm models like Freundlich, Langmuir and Temkin were examined. Monolayer biosorption is well explained by Langmuir isotherm whereas biosorption onto a heterogeneous surface was well illustrated by Freundlich isotherm[15] .Correlation Coefficients of Freundlich, Langmuir and Temkin are tabulated in Table-4.

Table-4: R^2 Values for Freudlich, Langmuir and Temkin Models

Models	R^2
Freundlich	0.9196
Langmuir	0.9108
Temkin	0.8952

Freundlich Adsorption Isotherm

Freundlich adsorption isotherm was checked. By using the graph the amount of dye adsorbed was calculated. Freundlich Isotherm model is used for multilayer adsorption between adsorbate and adsorbent[16].

The heterogeneous biosorbing surface was explained by Freundlich and he further describes the vacant sites with distant energies[17]. The intensity of biosorption of a sorbent was given by this model. The empirical equation of this isotherm is:

$$\log qe = \log Kf + 1/n \log Ce$$

Where, Kf and n are constants with n indicating the biosorption process and n also indicates that the process is highly favorable, Kf $((mg/g)(L/mg)^{1/n}$ the biosorption capacity. Fig.-5 shows that the Freundlich isotherm was found to be linear and the correlation coefficient factor was found to be 0.9196. It was suggested that Freundlich Isotherm fits the experimental data and confirms the multilayer coverage on the adsorbent.

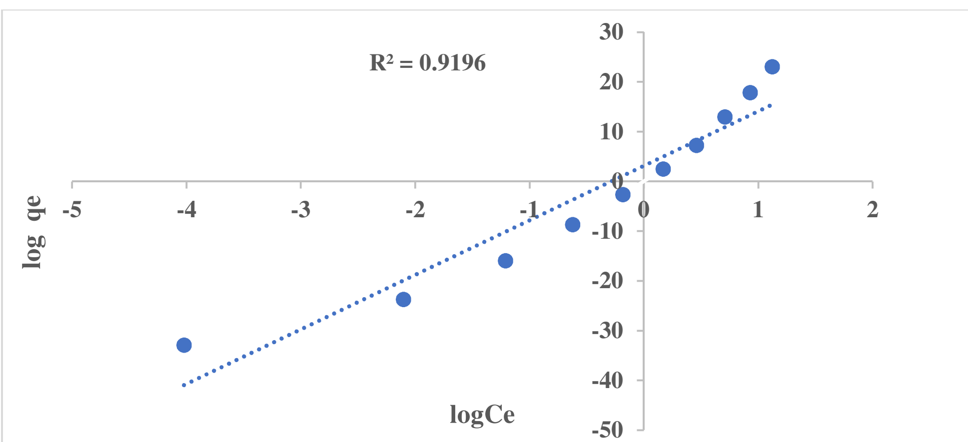

Fig.-5: Graph Showing log qe Vs log Ce

Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm model suggests that adsorption occurs on homogeneous sites within an adsorbent based on the assumption that each molecule possesses constant enthalpies and sorption activation energy[18].The equation is:

$$C_e/q_e = 1/k_l q_m + 1/q_e Ce \quad (2)$$

Where Ce is a biosorbate concentration (mg/L), qe is the quantity of biosorbate adsorbed (mg/g), k_l and q_m are constants of biosorption rate and capacity of biosorption. Langmuir isotherm was represented by plotting. In Ce with Ce/qe and slope of $1/q_m$ was obtained.

Langmuir model is achieved and this is proved by the linearity in the graph. The R^2 value for RY-14 was obtained as 0.9108. It was found that R^2 value of Langmuir isotherm was lower than Freundlich isotherm, which confirms the multilayer coverage of RY-14 onto ABLP.

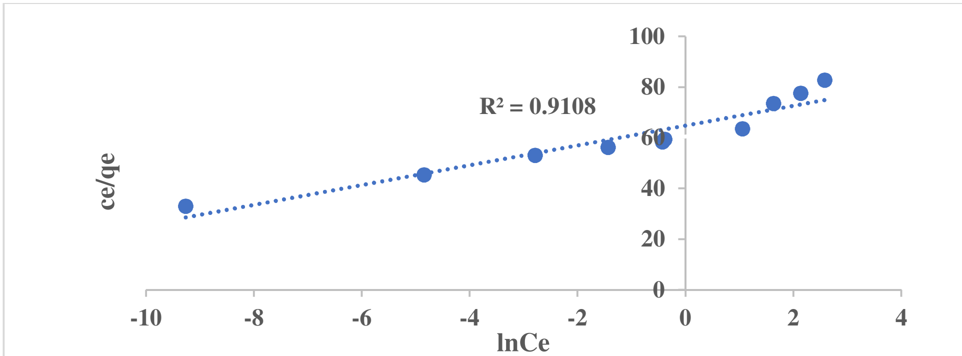

Fig.-6: Graph Showing C_e/q_e Vs ln Ce

Temkin Isotherm

The equilibrium data was further applied to Temkin isotherm model. The Fig.-7 represents the linear plot of logCe Vs qe of the Temkin isotherm.

It can be seen from the figure that R^2 value for the adsorption was found to be 0.8952 which is comparatively lesser than other two models and shows that Temkin isotherm model was inapplicable.

The data of biosorption is analyzed as:

$$q_e = B_T \log (A_T) + B_T \log (C_e) \quad (3)$$

Where, A_T and B_T are the Temkin constants. B_T=RT/b; A_T= e (intercept/B_T); (R =8.314 J/mol K), T is temperature represented in Kelvin.

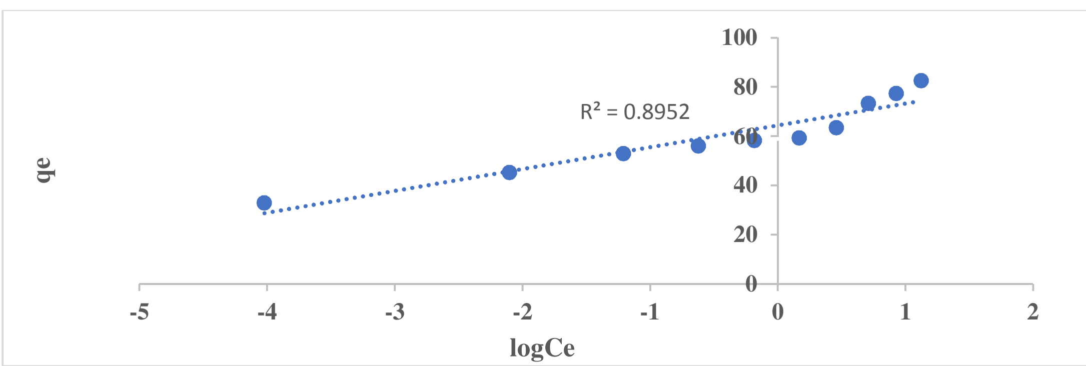

Fig.-7: Graph Showing q_e Vs log Ce

Kinetics of Adsorption

The experimental data were tested with pseudo first order kinetic model.The kinetics of RY-14 adsorption on ABLP was studied with respect to different concentrations of dye solutions.

The rate constant is the plot of log 1-U(t) Vs contact time and is shown in Fig.-9. The Kinetic equation of first order is given by:

$$\ln(1-U(t)) = -kt \quad (4)$$

$$Ut=\frac{CA-CA(t)}{CA-CA(e)} \quad (5)$$

Where, CA=initial concentration CA(t)=concentration at time 't' and CA (e)=equilibrium dye concentrations for first order reaction. The slope indicates the rate constant (K) of the reaction. First order kinetics is proved by the graph and a straight line was obtained.

SEM Analysis

Scanning Electron Microscopy studies were performed to characterize the surface morphology of the biomass before adsorption. Figure-10 shows the SEM image of ABLP before adsorption. ABLP has a considerable heterogeneous surface with a considerable number of cavities and more pores that can act as an excellent binding site for the dye adsorption[19].

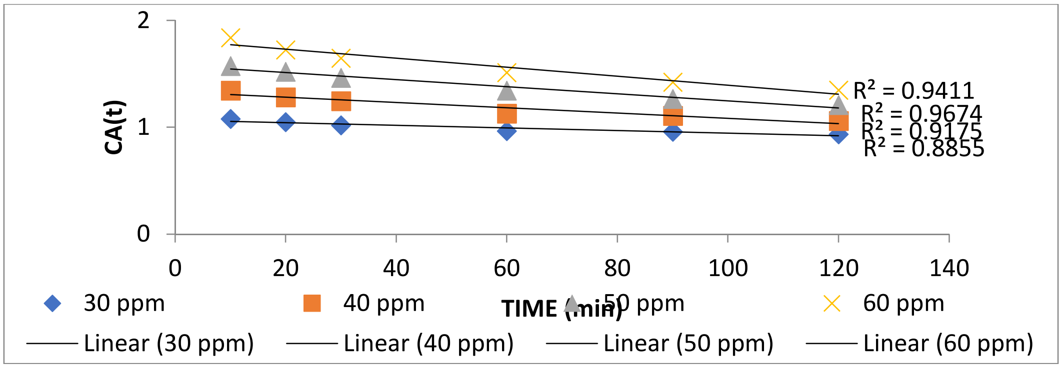

Fig.-8: Graph Showing Time Vs CA (t)

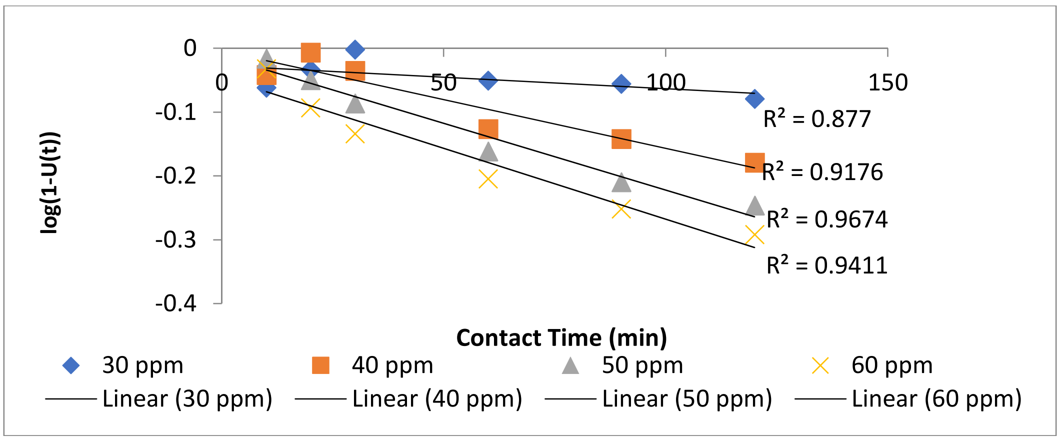

Fig.-9: Graph Showing Contact Time Vs log (1-U(T))

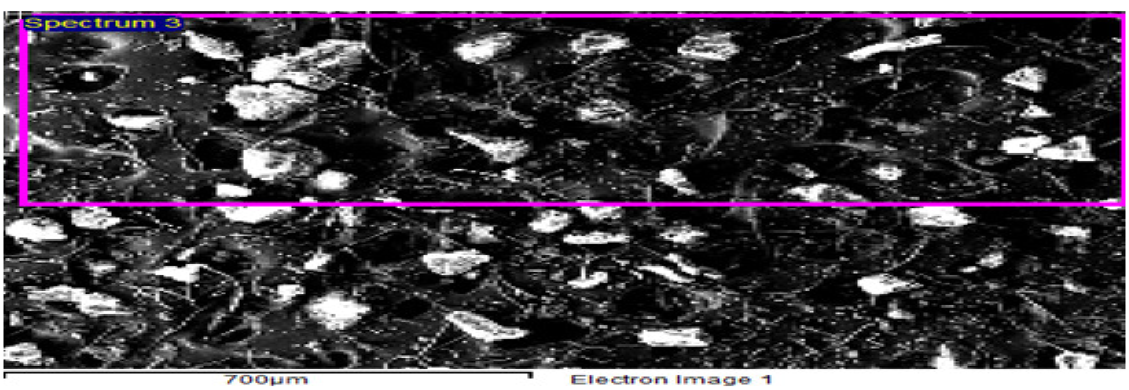

Fig.-10: SEM Analysis of ABLP (700µm)

CONCLUSION

It is concluded that ABLP could be used to remove RY-14dyefromaqueoussolution.The optimum pH was observed at 2.As the sorbent dose was increased, the percentages of dyes sorbed was also increased and reached maximum value. The adsorption equilibrium was achieved at 4 hours. It was proven that Freundlich isotherm fit well. The adsorption processes followed the pseudo-first-order rate kinetics. When we justify the results shown above we could conclude that *Averrhoa bilimbiis* an effective dye adsorbent from aqueous solutions. *Averrhoa bilimbi* leaves-based adsorbent offers many attractive features such as outstanding adsorption capacity for RY-14 dye, low in cost and environmental friendly. It offers significant advantages over currently available adsorbent and in addition, it contributes to agricultural waste minimization strategy.

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