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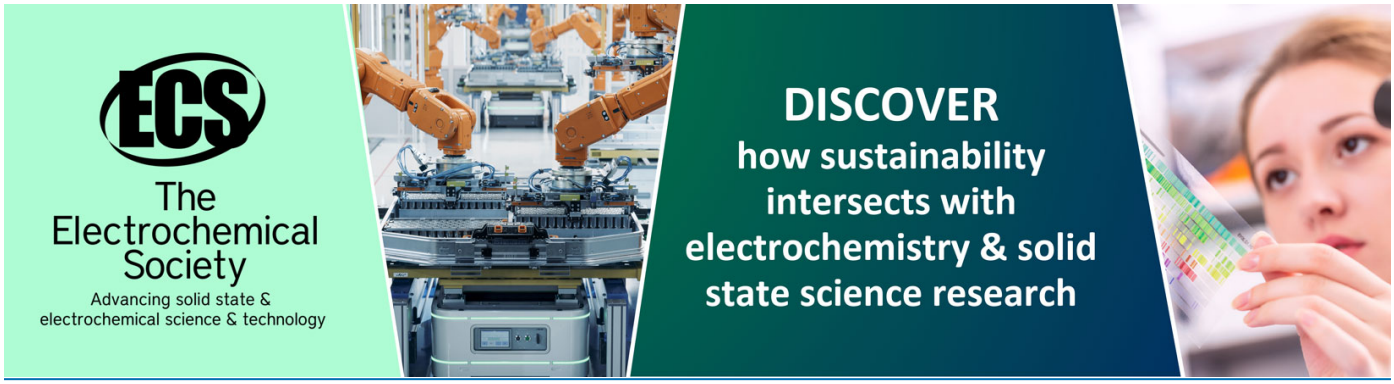

Removal of methylene blue (MB) from waste water by adsorption on jackfruit leaf powder (JLP) in continuously stirred tank reactor.

T Ahmed[1], W Noor[1], O Faruk[1], M C Bhoumick[1] and M T Uddin[1]

Department of Chemical Engineering and Polymer Science, Shahjalal University of Science and Technology, Sylhe-3114, Bangladesh.

E-mail: mcbhoumick.sust@gmail.com

Abstract. Dye contaminated waste water possess serious threat to the goal of reaching sustainable environment. Bio adsorbents can be utilized very effectively in removing dye ingredient from wastewater due to their high kinetics and capacity. The study was focused on observing bio adsorbent (jackfruit leaf powder) activity for Methylene Blue adsorption in a Continuous Stirred Tank Reactor (CSTR) for wastewater treatment.Batch and kinetic study of adsorbent were performed. The maximum adsorption capacity at equilibrium was found to be 271 mg/g and adsorption followed Langmuir isotherm. The kinetics study provided evidence of instantaneous adsorption while the zero point charge of the adsorbent was 3.9. The FTIR of the JLP-MB system was carried out to explain the adsorption phenomena with representing groups. The CSTR study was performed under various parameters such as, effect of flow rate, adsorbent dosage, CSTR arrangement and initial concentration. The dye stream first treated in 1st reactor and then its effluent passes into the 2nd reactor and treated again. It was found that the single CSTR removes 30-45 % of the dye depending on the initial concentration, while the series effect removes 70-85 % of the dye overall.

1. Introduction:

Water is the foundation of life on planet and one of the most important constituents of modern industrialization. Considering both volumes discharged and effluent composition, the wastewater generated by the textile industry was rated as the most polluting among all industrial sectors [1, 12]. Many types of dye are used in textile industries such as direct, reactive, acid and basic dyes. Most of these dyes represent acute problems to the ecological system as they considered toxic and had carcinogenic properties, which make the water inhibitory toAquatic life [6]. The effluents from dye manufacturing and consuming industries are highly colored coupled with high chemical and biochemical oxygen demands (COD and BOD) [2]. Discharge of such effluents imparts color to receiving streams and affects its aesthetic value.Color hinders thepenetration of sunlight into waters, retards photosynthesis, inhibits the growth of aquatic biota and interferes with gas solubility in water bodies [9]. Dyes may also be problematic if they are broken down anaerobically in the sediment, as toxic amines are often produced due to incomplete degradation by bacteria [7]. Dyes laden wastewater is usually treated by physical or chemical processes. All of these methods have different color removal capabilities, capital costs and operating rates. Among these processes, adsorption has been found to be superior to other techniques for wastewater treatment in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances [9]. A small amount of adsorbent can adsorb

adequate amount of adsorbate. Commercial activated carbon is an excellent adsorbent in terms of adsorption capacity but due to its high cost, adsorbents derived from cellulosic sources are extensively studied. Researchers have investigated dye removal from aqueous solutions using natural materials or agricultural wastes such as palm shell [17], coconut coir[18] sawdust[19], jute fiber[20], rice husk[21]mango leaf powder [22]etc. as low cost biosorbents[16]. In this present study Jackfruit leaf powder (JLP) was used as an adsorbent for MB adsorption. The present study was mainly focused on how to treat dye containing waste water by adsorption via bio adsorbent in Continuous Stirred Tank Reactor (CSTR). CSTR was advantageous over batch or column system in removal of waste constituents from wastewater stream because of continues steady state operation. The objective of this study was to find an efficient method of dye removal from waste water in continuous basis by series CSTR system for MB-JLP adsorption as a model.

2. Experimental Methods:

2.1 Materials:

Jackfruit leaf powder was used to study adsorption of methylene blue in CSTR. Leaves were collected from local area. After collecting the leaves, they were thoroughly cleaned to remove dirt and other earthy particles. Then the leaves were dried in oven at 105^{o}C overnight. Dried leaves were crushed and boiled in water until the removal of its mostlignin and coloring components. Boiled leaves then filtered and dried in oven at 105^{o}C for 24 hours and sieved to particles size 45-500µm and stored in a plastic jar for using as an adsorbent.Methylene Blue (Fig-1) was purchased from Merck and used as received without further purification. The stock solution of MB was prepared with a concentration of 1000 ppm (1000mg/L) and all other working solutions were prepared by diluting the stock solution with distilled water.

2.2. Methods:

To study the effect of important parameters e.g. adsorbent dosage, initial dye concentration, and contact time [1, 3] on the adsorptive removal of MB, batch experiment was conducted on 25±2^{o}C. In this study six 250 ml stopper bottles were used. Each of them was filled with 200 ml of methylene blue solution of seven different concentrations. A fixed amount of adsorbent was added to each solution. The samples were then shaken with a flask shaker (Stuart Scientific Co. Ltd, Model: SF1, UK) at 450osc/min for 6hrs. Within this time the system reached equilibrium. The solutions were then centrifuged for 5-10 min to settle down the adsorbent. The dye solution was then separated and the concentration of the solution was determined with UV-vispectrophotometer (UV-2600 PC, Manufacture: shimadzu, Made in Japan) at 664 nm wavelength.

The adsorption density q_e can be expressed as

$$q_e = \frac{V(C_0 - C_e)}{W} \quad \text{.....1}$$

Where, C_0 and C_e are the liquid phase concentration (mg/L) of MB at initial time and any time t respectively. V was the volume of the solution (L) and W was the mass of the adsorbent (gm).For adsorption isotherm, where the equilibrium density q_e (mg/gm) was calculated by Eq (1).Theoretical equation for calculating solute (adsorbent) concentration on the CSTR and outlet with time was;

$$(C_{in} - C) = (C_{in} - C_0)\, e^{-\frac{t}{\tau}} \quad \text{.....2}$$

If no solute was fed to the CSTR with inlet stream then $C_{in} = 0$ and equation 2 reduces to,

$$C = C_0 e^{-\frac{t}{\tau}} \quad \text{.....3}$$

During single CSTR operation; initially the CSTR was filled with a dye solution of a fixed concentration up to the outlet pipe where total solution volume was 2L. Fixed dose of adsorbent W

(gm/L) was added to the CSTR at time t=0. Dye solution from the storage tank was added to the CSTR at a constant flow rate. The flow rate was maintained with the help of a valve. The adsorbent concentration in the CSTR was kept constant by adding the amount lost every 5 minutes. This amount was calculated from Eq. (3). The overflow solution was collected every 5 min and centrifuged to settle the adsorbent. The sample was then taken into test tube and the concentration was measured with UV-vis spectrophotometer. Effluent was passed through the discharge of 1st CSTR.When two CSTR are in series operation; steps are the same as single CSTR operation. But rather passing all effluent from 1st CSTR through discharge, the stream was directed into 2nd CSTR by closing ball valve of 1st CSTR discharge. When 2nd CSTR was filled with effluent of 1streactor, same previous steps were maintained as single CSTR for 2nd reactor too.

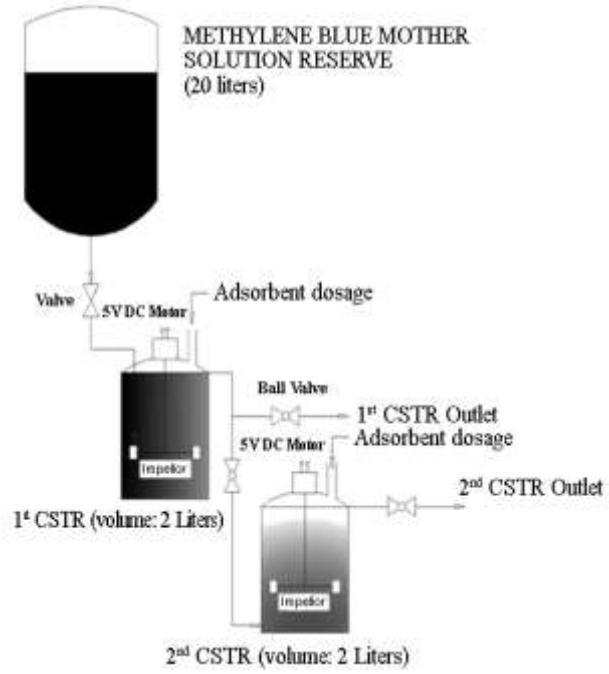

Figure 1. Complete diagram of series CSTR system for adsorption of MB onto JLP

3. Results and Discussion

3.1. Particle size distribution

Particle size distribution was measured by sieve shaker (Vibratory Sieve Shaker, Analysette) of five sieve size tray (500, 250, 125, 63, 45 µm). 30gm adsorbent was put in the shaker and run for 3 hours. And the remaining on the top of sieve tray was weighted carefully. The distributions of particle size are shown on figure 2.

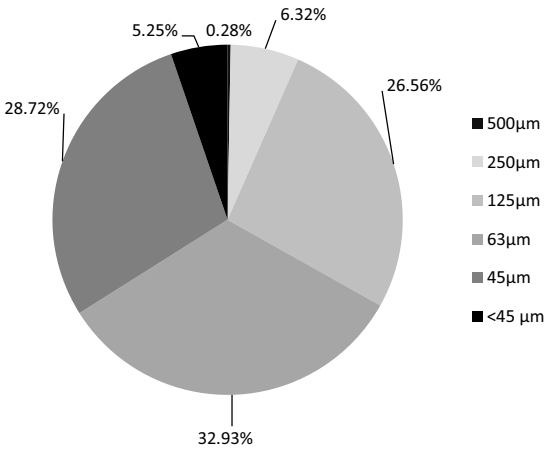

Figure 2. Particle size distribution

3.2. Zero Point Charge

The surface charge, Q was calculated from the experimental titration data according to the following equation

$$Q = 1/w\ (C_A - C_B - [H^+] - [OH \quad \text{.....4}$$

where, w- dry weight of adsorbent in aqueous system (g/L); C_A is the concentration of added acid in aqueous system (mol/L); C_B is the concentration of added base in aqueous system (mol/L); $[H^+]$is the concentration of H^+(mol/L); $[OH^-]$ is the concentration of OH^- (mol/L). The pH value at the point of zero charge was then determined by plotting Q versus pH.The plot on figure 3 illustrates the surface charge property of JLP adsorbent particles. It was found that at pH 3.9 the net charge on the JLP surface was zero. Above 3.9 the surface charge is negative and below vice versa. MB is a positive type of dye, hence higher pH favors adsorption.

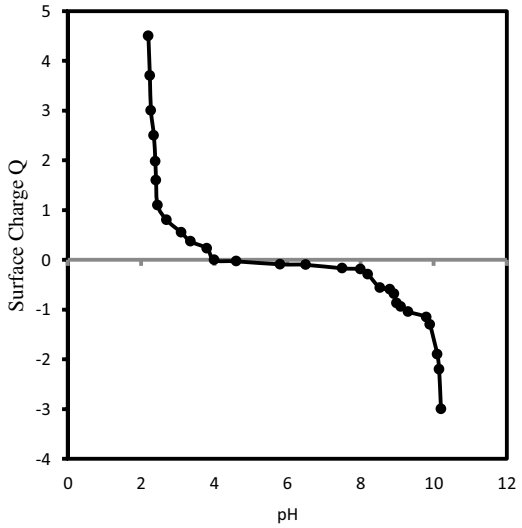

Figure 3. Zero Point Charge of JLP adsorbent.

3.3. Fourier Transform Infrared Spectroscopy of adsorbent

The FTIR spectrums of JLP before adsorption of MB are shown in Figure 4 and that of JLP after adsorption are revealed in Figure 5. As shown in Figure 4 the spectra display a number of absorption peaks, indicating the multifaceted nature of the material examined. The FTIR spectroscopic analysis dictated broad bands at3418 cm^{-1}, representing bonded OH groups[11]. The band observed at 1743 cm^{-1} was assigned to a carbonyl band (CO) of pectin ester[15], while the peak at 1616 cm^{-1} was attributed to C=O stretching of carboxylic acid with intermolecular hydrogen bond. The peak observed at 1520 $cm^{-}1$ corresponds to secondary amine group[16].FTIR analysis indicates that JLP was represented by functional group OH, COOH, NH, CO, that could be potential adsorption site for MB.

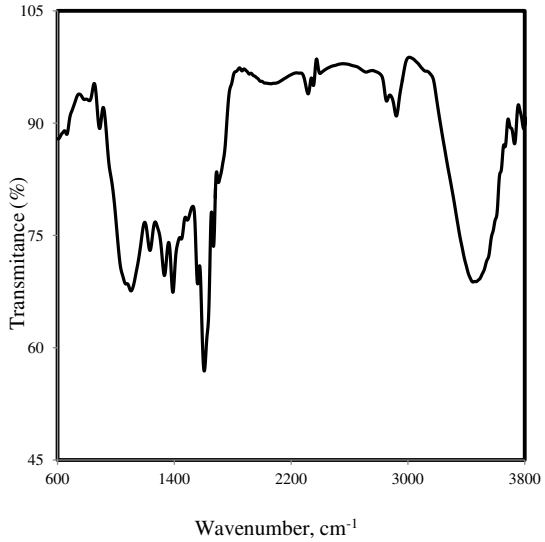

Figure 4. FTIR of JLP before adsorption

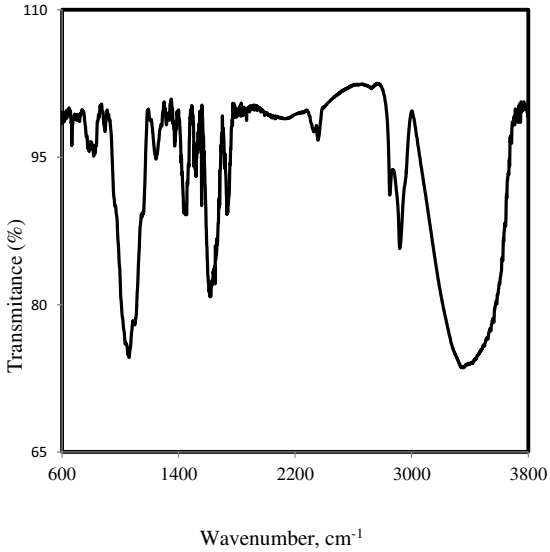

Figure 5. FTIR of JLP after adsorption

3.4. Adsorbent Capacity

In batch study, it was seen that with increasing concentration of MB solution, the capacity of adsorbent tends to increase. In the figures 3and 4, it shows that capacity increases with growing concentration; capacity increases for a certain amount adsorbent dosage.

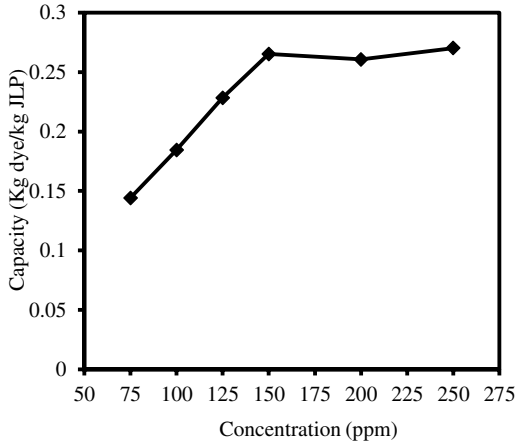

Figure 6. Adsorbent capacity vs. initial dye concentration (Volume of solution = 200ml, adsorbent added = 0.1gm, initial concentration 75, 100, 125, 150, 200, 250ppm)

3.5. Langmuir Adsorption isotherm:

The Langmuir adsorption isotherm was valid for monolayer adsorption onto a surface containing a finite number of ideal sites. This model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The Langmuir adsorption isotherm for solid-liquid adsorption system was represented by the following equation

$$\frac{1}{q_e} = \frac{1}{q_\infty K} \cdot \frac{1}{C_e} + \frac{1}{q_\infty} \quad \text{.....5}$$

Where, q_∞ and K was the adsorption capacity (Kg adsorbate/Kg adsorbent) and rate of adsorption respectively. A plot of the $1/q_e$ vs. $1/C_e$ was for MB adsorption on JLP was presented on Fig 6. The Langmuir constant are calculated by equation 5 and tabulated in Table-1. Form Figure 7, it can be seen that adsorption of MB onto JLP was best fitted with Langmuir isotherm. The maximum sorption of JLP for MB was found 271mg/gm. Table 2 shows a comparison of other low cost adsorbent for uptake of MB.

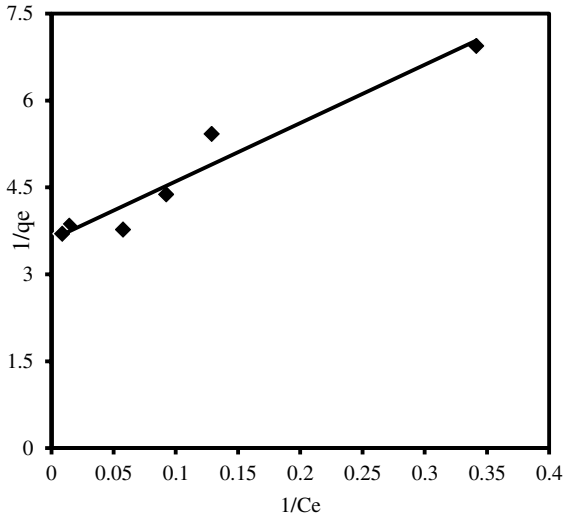

Figure 7. Langmuir isotherm for methylene blue adsorption onto JLP (Volume of solution = 200ml, adsorbent added = 0.1gm, initial concentration 75, 100, 125, 150ppm, Temperature 24±2^{o}C)

Table 1. Langmuir isotherm constants

System	q_∞ (kg/kg)	K (m^3/kg)	R^2
MB-JLP	0.271	0.3307	0.95

Table 2. Adsorption capacity of different adsorbents found in literature

Adsorbent	Capacity (mg/gm.)	Authors
Bio-sludge ash	1.599	(Chih-Huang Weng, 2005)
Activated carbon of rattan sawdust	294.1	(B.H. Hameed A. A., 2006)
Cedar sawdust	142.36	(Hamdaoui, 2006)
Crushed brick	96.61	(Hamdaoui, 2006)
Bituminous coal-based activated carbon	588	(Emad N. El Qada, 2006)
Peanut hull	68.03	(Renmin Gong, 2005)
Clay	58.2	(A. Gürses, 2003)
Jackfruit leaf powder	271	Present Study

3.6. Kinetics Study

Effects of contact time on adsorption of dye were studied for the different initial concentration of dye with fixed Adsorbent dosage Figure 8 represents methylene blue JLP system. It was seen from the figure that the initial rate of adsorption was high for both the system and 70-85% of dye was removed within first 10 min of adsorption. It represents adsorbent's high kinetic ability. After that, the rate was decreasing gradually leading to equilibrium. This was due to the high capacity of the adsorbent and the availability of dye molecules at the adsorbent interface. When the surface active sites of adsorbent are covered fully, the extent of adsorption reaches to a limit resulting in saturated adsorption.

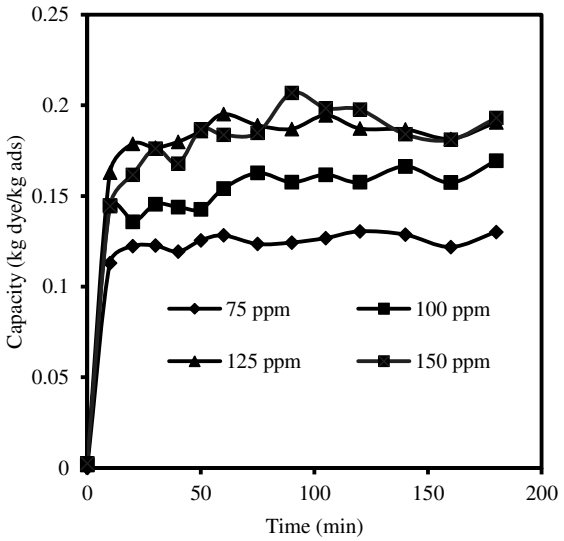

Figure 8. Kinetics study of Methylene blue adsorption onto JLP. (Volume of solution = 200ml, adsorbent added = 0.1gm, initial concentration 75, 100, 125, 150ppm, Temperature 25±2^{o}C; shaking speed = 350 osc. /min)

4. CSTR performance study

4.1. Single CSTR Study

For this study, a fixed amount of adsorbent (1gm.) was used. Adsorbent makeup dosage varied with flow rate. Higher the flow rate, higher the makeup dosage. Adsorbent make up dosage was calculated by equation 3. For single CSTR, performance was studied for three different flow rates and every time, the reduced concentration of effluent dye was in the desired range with satisfactory dye removal. In this study, initial adsorbent dosage was maintained all over the reactor operation. And make up dosage was applied in every five minutes after the sample withdrawal.

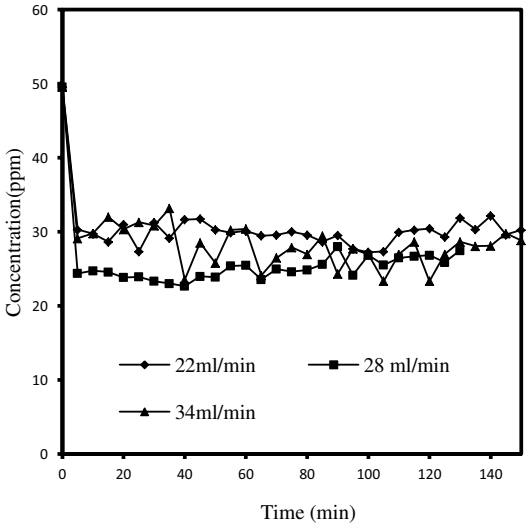

Figure 9. Effluent concentration curve of Single CSTR operation for adsorption of MB onto JLP.

4.2. Series CSTR Study

Two equal volume CSTR was connected in series to see the overall removal of MB. Effluent from 1st CSTR enters into the inlet of 2nd CSTR. Same parameters (flow rate, adsorbent make up dosage) were cautiously maintained in both reactors to get the performances equally. It was seen that, series effect increases the removal of methylene blue quite significantly. While the first reactor removed 40-50 % of the initial dye, with the addition of second one the removal percentage ascended to around 75-90%. Figure 10 summarizes the whole study.

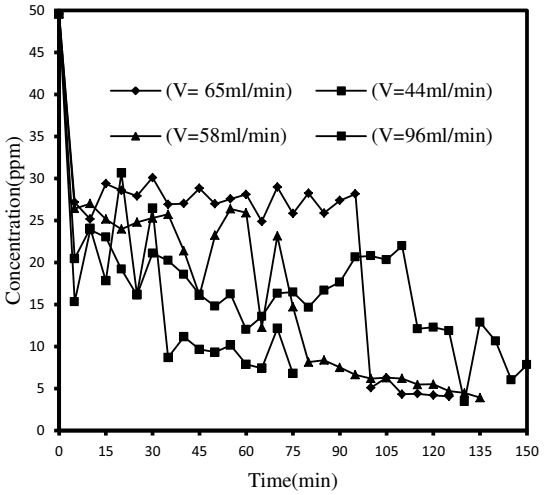

Figure 10. Series CSTR operation for fixed amount adsorbent for adsorption of MB onto JLP.

5. Conclusions

This study was primarily focused on finding an alternative potential system to treat wastewater by adsorption with high rate and efficiently in CSTR. Due to continuous steady state mode of operation of CSTR; for adsorption purpose, it was required to use an adsorbent with high kinetics and sorption capacity. Jackfruit leaf powder (JLP), for its high kinetics, and comparatively high capacity makes it an outstanding choice for using in CSTR system for treating dye from the waste stream. It was found that, in CSTR, adsorption can be possible with a considerable ease by using low-cost natural adsorbent. According to Langmuir isotherm, MB adsorption on JLP was favorable. The maximum sorption capacity of MB onto JLP has been found 271mg/gm. it was relatively higher than other natural low-cost adsorbent except for activated carbon. Other adsorbent with higher kinetics and capacity can be used in CSTR to treat dye containing waste stream by adsorption method easily and proficiently.

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