A Study on Adsorption Process by Activated Rice Husk by Using Crystal Violet as Dye by Spectrophotometric Method

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Abstract:

Activated Rice Husk (ARH) was used as adsorbents for decolourisation. ARH was prepared from rice husk treated with nitric acid. The adsorption capacity was evaluated for the decolourisation of waste water containing crystal violet. The effect of system variables such as pH is ignored because of variation in colour of solution with pH however contact time and adsorbent dose were investigated. The result shows that efficiency varies with the variation in adsorbate concentrations and adsorbent. Colour removal efficiency was found to be 88 % to 94 % at the dose of 20 g/L for ARH. The studies were carried out at crystal violet concentration of 50 mg/L, 30 mg/L and 10 mg/L. On the basis of adsorption isotherm graphs, R-square values were determined and found to fit the adsorption data. The Freundlich adsorption isotherms are good fitted for the experimental data.

Keywords: Rice husk, ARH, Crystal violet, Adsorption isotherms

Introduction:

In the light of industrialization and urbanization, pollution is a serious problem ever since sewage and industrial effluents are disposed into the water bodies and on land. The wastewater contain a wider variety of materials of both organic and inorganic nature including toxic substances and are usually discharged with or without treatment into the surface water such as rivers, streams, lakes or into oceans or on land or in sewers. One of the most common water pollutant is colour. They find their way into the water by the discharge of dyes from paper and pulp industries, textile industries, tanning [1] industries and many other industries. Colors in the water affect the nature of water, inhibit sunlight penetration and reduce photosynthetic action. Some of the dyes cause rapid depletion of dissolved oxygen affecting aquatic life adversely. Some of the dyes are toxic and carcinogenic. Thus, uses of dye contaminated water without any treatment may cause adverse effect on human health, domestic animals, wildlife and on the environment. So it is necessary to treat or remove color from the wastewater before discharge. Various treatment methods for removal of colour and dye are co-agulation using alum, lime, ferric chloride and ferric sulphate, oxidation, flocculation, ozonation, biological treatment, adsorption and membrane processes [2]. Among these methods, adsorption method appears to offer the best prospect for overall treatment of colour removal [3],[4]. Use of Granulated Activated Carbon (GAC) or Powdered Activated Carbon (PAC) is more common[5], [6]. However, they are expensive and the regeneration or disposal of it has several problems. Thus, to make the process customer friendly, the use of several low cost adsorbents has been studied. Locally available natural material can minimize or avoid the concerns and significantly reduce treatment cost[7]. Being India an agricultural country, a large amount of agro-waste is generated every year. The use of these agricultural solid wastes such as coir pith, banana pith, coconut shell, rice husk and straw, bagasses, saw dust, bamboo dust, groundnut shell, etc. as an adsorbent for removal of colour from wastewater will be customer friendly[8]. Rice is the second largest produced cereal in the world. Worldwide, India stands first in rice area and second in rice production, after China[9]. During milling of paddy about 78 % of weight is received as rice, broken rice and bran. Rest 22 % of the weight of paddy is received as husk[10]. The total quantity of rice husk produced annually in the country is about 29.5 million tones[11]. The possible utilization of rice husk as an adsorbent for crystal violet dye or other colour from aqueous solutions can be investigated because of its effective adsorption properties[12-16].

Materials and Methods

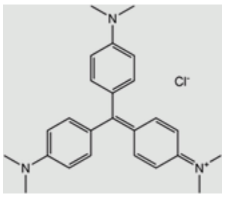
a. Collection and Preparation of Adsorbents

Rice husk were collected from Shriram rice mill situated in Chandrapur district of Maharashtra state. The rice husk was screened and washed with water to remove the dirt and was sun dried for a day. Then the dried rice husk was soaked in 2.0 mol/L of nitric acid for an hour. It was then rinsed with distilled water for 2-3 times and oven dried at 105°C for 2 hours. The oven dried rice husk was ground and sieved through BSS-30 mesh size particle. The name given to the adsorbent was Activated rice husk (ARH).

b. Preparation of dye solution

The molecular formula of crystal violet if $C_{25}N_3H_{30}Cl$, when dissolved in water the dye has a blue-violet colour with an absorbance maximum at 590 nm and an extinction coefficient of 87,000 $M^{-1}cm^{-1}$.The colour of the dye depend on the acidity of the solution. At a pH of 1.0 the dye is green with absorption maxima at 420 nm and 620 nm while in a strongly acidic solution (pH of −1), the dye is yellow with an absorption maximum at 420 nm. The different colours are a result of the different charged states of the dye molecule. In alkaline solutions, nucleophilic hydroxyl ions attack the electrophilic central carbon. This effect produces a slight fading of the yellow colour.

It was chosen because of its known strong adsorption onto solids. The dye is regarded as acutely toxic, but it can have various harmful effects. The structure of crystal violet is as given below:



Crystal violet (Thomos Baker) was collected from laboratory. The stock solution of dye was prepared by dissolving 10 g of crystal violet in 1000 ml of distilled water. The working solutions were prepared by serial dilution of this stock solution.

c. Equipment

The Spectrophotometer (Elico 102S) was used for Crystal violet analysis. The rotary shaker (model K-201, manufactured by BESTO), pH meter (Equiptronics), Centrifuge machine (REMI R8C laboratory centrifuge), etc. were used for all adsorption experiments.

d. Experiments

The working solution of different concentrations 50 mg/L, 30 mg/L, and 10mg/L were prepared by serial dilution of stock solution. The Three factors initial concentration of dye, contact time and adsorbent dose were varied. The batch adsorption tests were carried out by shaking 100ml working dye solution in a stoppered conical flask. The conical flasks were placed on rotary shaking machine for one hour at 150 rpm. The progress of adsorption during the experiment was determined by removing the flask after desired contact time, centrifuging and analyzing the supernatant solution spectrophotometrically at 590 nm. Adsorption tests were performed at temperature 29°C ±2. The spectrophotometric readings were recorded and further calculations were done to see the removal efficiency of the adsorbents. The removal efficiency was calculated using following formula:

$$Removal\ efficiency, \%\ \eta = \frac{(C_i - C_f)}{C_f} \times 100$$

Where, C_i is the initial concentration of crystal violet in solution and C_f is final concentration of crystal violet in solution. Adsorption isotherms were used to model colour adsorption. The adsorption isotherms were tried to fit to the experimental adsorption data. The isotherms used in this study were:

i. Freundlich Adsorption Isotherm

$$\frac{x}{m} = k \times C^{\frac{1}{n}} \qquad ----------1$$

Here, K is the measure of the capacity of the adsorbent (mass of adsorbate/ mass of adsorbent) and n is a measure of how affinity for the adsorbate changes with changes in adsorption density. Evaluation of the coefficient k and n can be accomplished using linearized form of equation 1.

$$\log\left(\frac{x}{m}\right) = logk + \frac{1}{n} logC$$

For Freundlich isotherm, graphs of $\log\left(\frac{x}{m}\right)$vis $logC$ were plotted.

The adsorption isotherms were tried to fit to the experimental adsorption data.

Linear regression analysis was conducted to determine the goodness of fit for the adsorption isotherms. Linear regression analysis was performed to determine whether the given isotherm is a good fit for experimental adsorption data. Based on the R-square values, the isotherm that explains the experimental adsorption data the best was selected.

Results and Discussions:

A. Effect of Contact Time

a) For different concentrations From Table 1 and Figure 1 for concentration 50 mg/L of crystal violet solution it is observed that the efficiency increases with increase in contact time. The efficiency is 84 % at contact time 60 minutes for ARH. After doubling the contact time i.e. 120 minutes the efficiency is reached upto 88 % for ARH . The difference is about 3-4 % only. Therefore, contact time was optimized at 60 minutes for 50 rng/L of crystal violet solution.

The efficiency is same for the concentration 30 mg/L of solution as that of concentration 50 mg/L of solution. Therefore optimum contact time is 60 min for concentration 30 mg/L of solution for ARH.

The equilibrium attained at 40 min for concentration 10 mg/L of solution for ARH. Therefore, considering concentration 10 mg/L of solution, the optimum contact time is 40 minute for ARH.

B. Effect of Adsorbent Dose

From Table 2 and Figure 2, it is observed that for concentration 50 mg/L of crystal violet solution the efficiency increases with increase in adsorbent dose. The efficiency is 65% to 93 % when the adsorbent dose varied from 2.5 g/L to 40 g/L for ARH. The efficiency is about 88 % for 20 g/L of ARH. Therefore, optimum adsorbent dose is 20 g/L of ARH for concentration 50 mg/L of solution.

From Figure 2 as compared to concentration 50 mg/L, for 30 mg/l of solution efficiency about 86 % is achieved at dose 10 g/L of ARH. At 20g/1 dose the efficiency is 91 %. The difference is of 5 %. Therefore optimum dose can be considered as 10 g/L of ARH. For concentration 10 mg/L of solution the efficiency is 93 % for 10 g/L of ARH as shown in Figure 2. The increase in efficiency is about only 1 % after doubling the adsorbent.. Therefore, optimized adsorbent dose is 10 g/L of ARH

C. Application of Adsorption isotherm

The R-square values of the linear regression performed were used to determine whether the isotherm was a good fit for the given experimental adsorption data. The R-square value close to 1 indicates a good fit by the model for the given experimental data whereas R-square value near 0 indicates that the model is not a good fit for the given experimental data. Freundlich Adsorption Isotherm From Figure 3 ,4 and 5, the Freundlich adsorption isotherm can be said to be good fit for the given experimental adsorption data, since the linear regression of log x/m vs log C gave R^2 values in the range of 0.87 to 0.98 for the different concentration of crystal violet.

Table. 1- Optimum Contact Time

Contact Time/minute	% efficiency of removal, %η		
	Conc. of CV*, 50mg/L	**Conc. of CV, 30mg/L**	**Conc. of CV, 10mg/L**
10	67	68	75
20	73	78	83
40	80	82	88
60	84	83	89
120	87	86	89
240	92	86	93

*Crystal Violet

Table. 2- Optimum Adsorbent Dose

Adsorbent Dose, g/L	% efficiency of removal, %η		
	Conc. of CV*, 50mg/L	**Conc. of CV, 30mg/L**	**Conc. of CV, 10mg/L**
2.5	65	81	89
5	72	80	92
10	80	85	93
20	88	91	94
40	92	93	94

*Crystal Violet

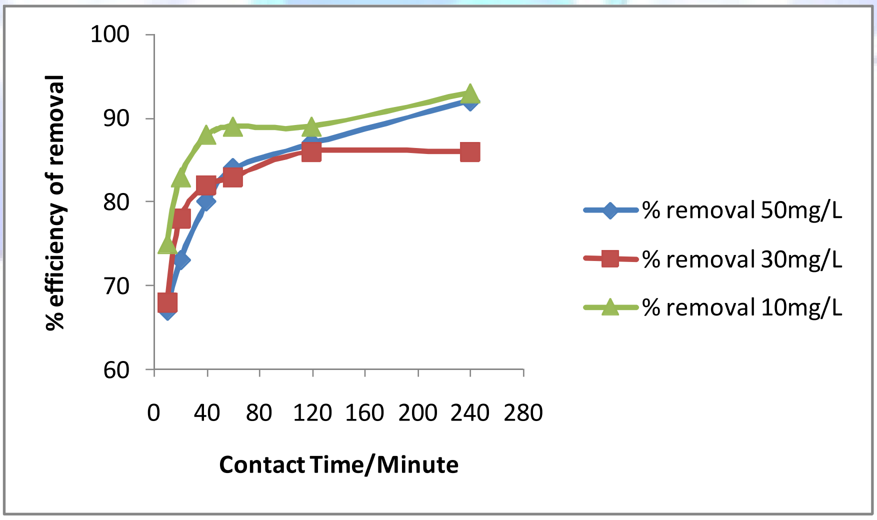


Figure. 1- Optimum Contact Time

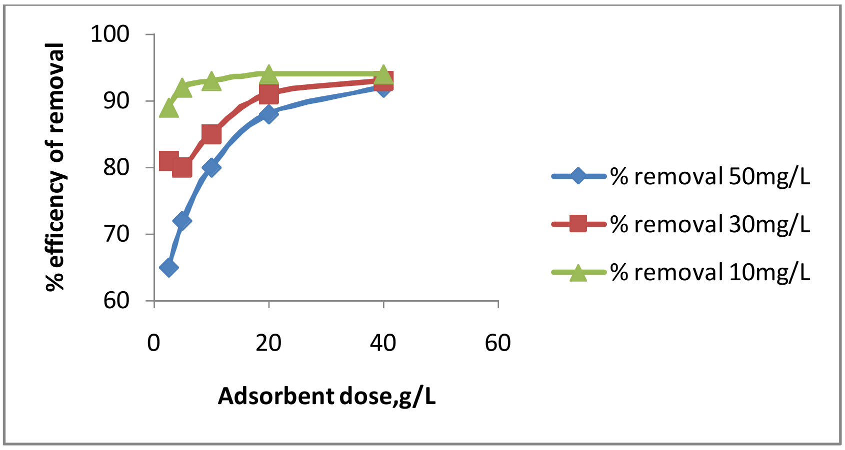


Figure. 2- Optimum Adsorbent Dose

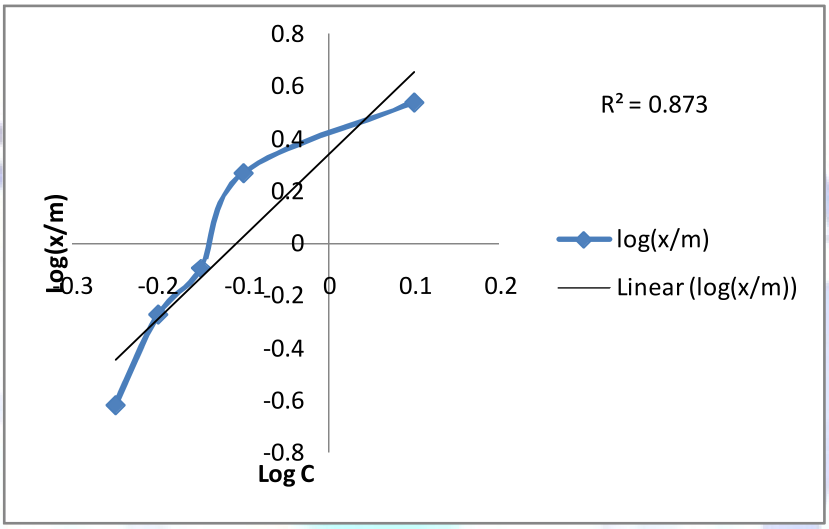


Figure. 3- Freundlich Adsorption Isotherm (50 mg/L)

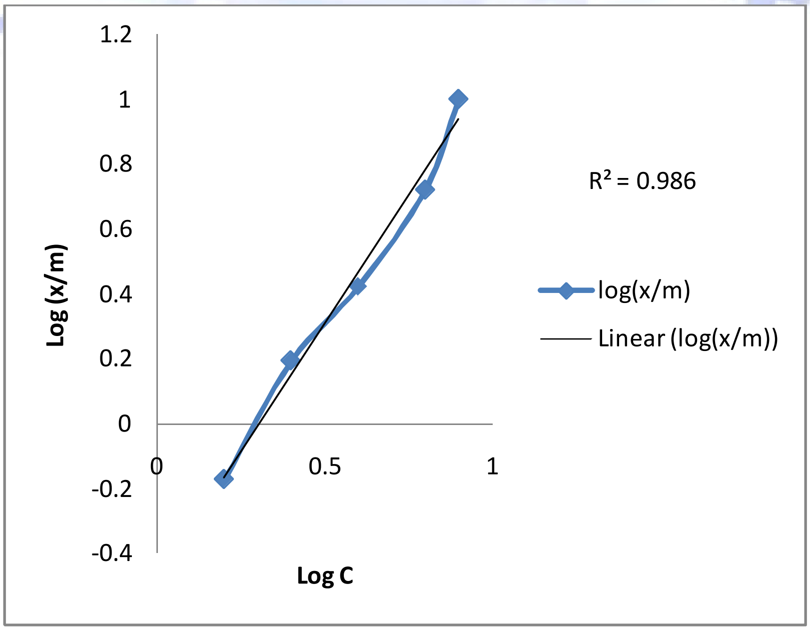


Figure. 4- Freundlich Adsorption Isotherm (30 mg/L)

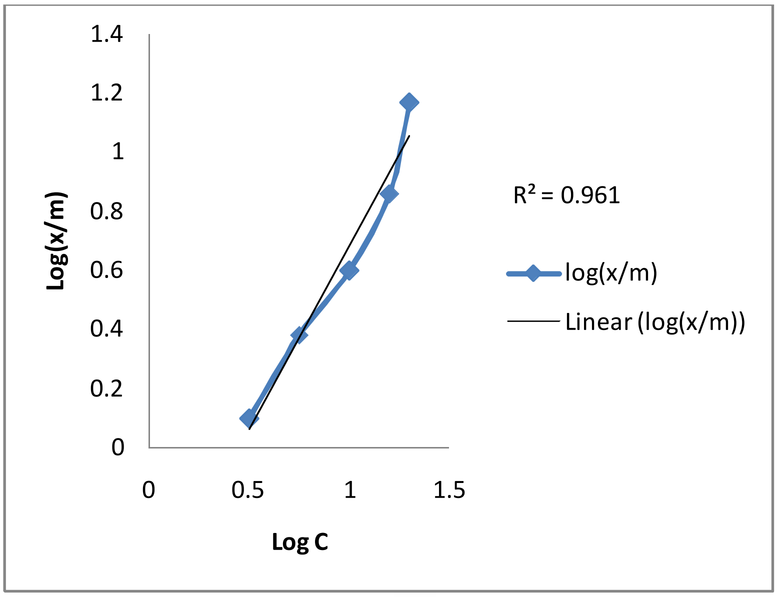


Figure. 5- Freundlich Adsorption Isotherm (10 mg/L)

Conclusion:

The result of present study clearly shows that acid treated rice husk is effective in removal of crystal violet and can provide an economical solution for removal of such colour from the aqueous solution. 88 % to 94 % colour removal efficiency can be achieved at the dose of 20 g/L of ARH having crystal violet concentration of 50 mg/L, 30 mg/L and 10 mg/L. The efficiency varies with the variation in adsorbate concentrations and adsorbent dose. From the results of the experiments conducted in present investigation, it is evident that experimental adsorption data for the adsorption of colour in this research can be explained by more than one adsorption isotherms. The result shows that the Rsquare values are closer to 1 for Freundlich isotherm models are good fitted to the experimental data. Thus full utilization of agro-waste and treatment of wastewater is one of the good prospective for good environment. The rice husk can be proved as good, effective and eco friendly adsorbent.

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