Adsorption Studies for Removal of Acid yellow 17 using Activated Rice Husk

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Abstract - ***Dyes are important particles in the textile and paper and pulp industries. But these dyes are harmful when this dyes combines with the water bodies because these dyes contains organic and inorganic toxic chemicals. They are harmful at low concentrations also and disturb the aquatic life. Various methods are in use for the removal of dyes from the wastewater. Adsorption is found to be low cost procedure in which the adsorbents are also easily available. In this study of adsorption activated rice husk was used as an adsorbent from the synthetic wastewater. The effects of various parameters such as pH, contact time, dosage of adsorbent and concentration of acid yellow 17 were checked for the removal of dye. The maximum amount of color adsorption efficiency was found to be 94.34 % at the dosage of 0.7 grams for the 20 ppm concentrated solution of acid yellow 17 taken in 100 ml of volume. The pH was maintained at 2 for the higher adsorption. The optimum contact time was found to be 80 minutes. Adsorption isotherms like Langmuir isotherm, and Freundlich isotherm were investigated for this adsorption studies. The adsorption study was followed Freundlich isotherm (R^2=0.996). The adsorption kinetics was investigated for the first and second order kinetics. Second order reaction was found to be good fit for the adsorption data (k=0.026).***

Key Words: *Rice husk, Activated rice husk, Acid yellow 17, Adsorption isotherms, Chemical kinetics*

1. Introduction

Now environmental pollution is causing very bad effects on human and plant ecosystems. Dye contamination increases the toxicity in the wastewater. The wastewater coming from the industries contain many numbers of toxic substances and are normally discharged with or without treatment into rivers, lakes, streams. Color is the most common water pollutant. These dye wastewater mixes with water bodies by the discharge from paper and pulp industries, textile industries, tanning industries, and other industries. The color inhibits the propagation of sun light in streams. It reduces photo synthesis action and also reduces dissolved oxygen. Dye contaminated water causes severe effects on human health, animals and environment. From all these points it is very essential to treat the wastewater before discharging to water bodies. Some of the treatment methods of color removal are coagulation with alum, ferric sulphate, ferric chloride, flocculation, ozonation, adsorption, membrane processes and biological treatments. Compared to all these treatment methods adsorption method becomes the best prospect for overall treatment for removal of color [1].

The existence of Acid yellow 17 dye in the wastewater effluents of textile industries, paper industries originates most harmful environmental problems to living organisms and they are highly toxic to humans and also for animals [2].

Adsorption becomes a good method for decolorization. This process has many advantages because of its sludge free clean process and maximum removing of dyes from the diluted solutions [3].

Very fewer efforts were carried out for the factorial design of adsorption process of rice husk for removal of dyes. Hence in this project work an attempt for the removal of acid yellow 17 dye from synthetic solution using activated rice husk. Various parameters on which the removal efficiency depends were examined. Those are pH, concentration of adsorbents, dosage of adsorbents, temperature effects were studied. The optimized value for the removal of pollutants was measured. Adsorption isotherms were carried out which includes linear adsorption isotherm, Langmuir isotherm, Freundlich isotherm were investigated. The adsorption kinetics studies were carried out.

2. Material and methodology

a. Collection and Preparation of Adsorbents

The rice husk was collected from rice mill. The collected rice husk was thoroughly screened and washed with distilled water. The dirty particles present in the samples collected were removed and then it was dried at sunlight for one day. The rice husk was sieved through a mesh of size of 150 micron. The rice husk was then dried in 100^0 C for the proper drying. After this the rice husk was soaked in 1N (One normality) solution of sulfuric acid for an hour at room temperature. The treated rice husk was then washed clearly using distilled water. The washed rice husk was kept in oven at 100^0 C for an hour. After this process the rice husk was kept in muffle furnace at 600^0 C for 2 hours.

b. Preparation of dye solution

The concentration of 1000 mg/L solution was prepared by adding 1 g of acid yellow 17 dye in 1000 mL of volumetric flask and adding the distilled water up to the mark.

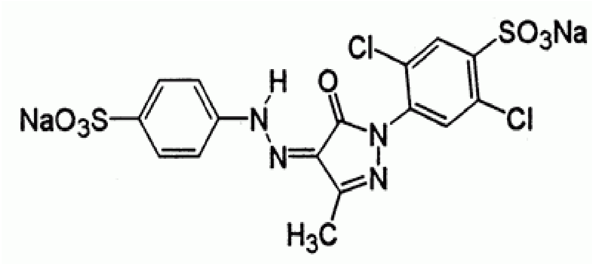

Figure 1: Chemical structure of acid yellow 17 [5]

Acid yellow 17 dye was used in this study of adsorption. Its molecular formula is $C_{16}H_{10}Cl_2N_4Na_2O_7S_2$. The molecular weight of acid yellow 17 is 551.29 and the color of dye is brilliant yellow. Normally it is available in powder form. It is soluble in water but slightly soluble in acetone. Acid yellow 17 dye is used for wool fabric printing, acetic acid bath of silk dyeing.

c. Experiments

The working solutions of different concentrations were prepared by the dilution of stock solution. The initial concentration, pH, adsorbent dosage, contact time and temperature was varied. Batch adsorption study was carried out in stoppered conical flask of 500mL with known adsorbent dosage and pH with required dye concentration. The conical flasks were kept in rotary shaker for 60 min at 150 rpm. After this contact time the conical flasks were removed. The solution was transferred to centrifuge for 15 minutes. The supernatant solution was analyzed for adsorption in a spectrophotometer. The spectrophotometer wavelength was kept at 418 nanometer [1].

The readings of spectrophotometer were recorded and calculations were carried out to find removal efficiency of the adsorbent. Following formulae was used for calculation of removal capacity or efficiency:

$$\% \text{ Removal efficiency} = \frac{(Ci - Cf)}{Ci} \times 100$$

Where, Ci is the initial acid yellow 17 concentration in solution and Cf is the final acid yellow concentration in the solution [1].

3. Results and Discussion

a. Effect of pH

In this study activated rice husk was used as adsorbent. In this adsorption study, the pH value was varied to observe the effect on adsorption of acid yellow 17 dye solution. The pH value was varied from pH 2 to 12 for a constant adsorbent dosage of 0.3 gram to a 100 ml volume of acid yellow 17 solution. The concentration of acid yellow 17 was maintained at 20 ppm. From the figure 2 the adsorption was maximum at lower pH values. At the pH of 2 the adsorption is maximum up to 72.11 %. Adsorption capacity decreases with increasing pH of the solution of acid yellow 17 dye.

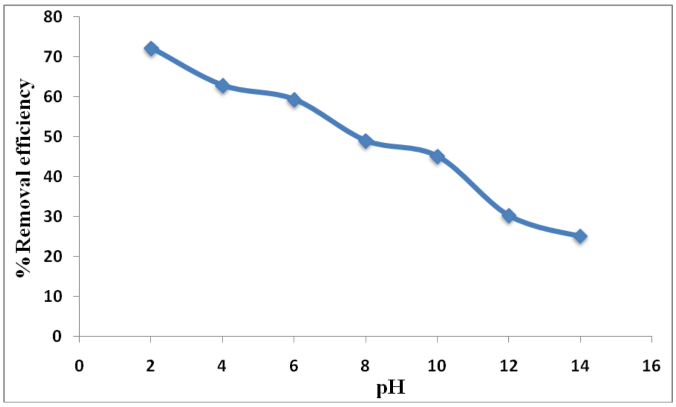

Figure-2: Effect of pH on Adsorption of acid yellow 17 dye on activated rice husk

b. Effect of adsorbent dosage

The adsorbent dosages were varied from 0.3 gram to 1.1 gram. The concentration of the solution was kept at 20 ppm and it was taken to a volume of 100 ml. The pH of solution was maintained at 2. The effect of dosage on percentage adsorption is as shown in figure 3.

The effect shows that as the adsorbent dosage was increased the percentage adsorption was also increased. The optimized value for which maximum adsorption was observed was 0.7 grams. The removal efficiency of 97.97 % was observed.

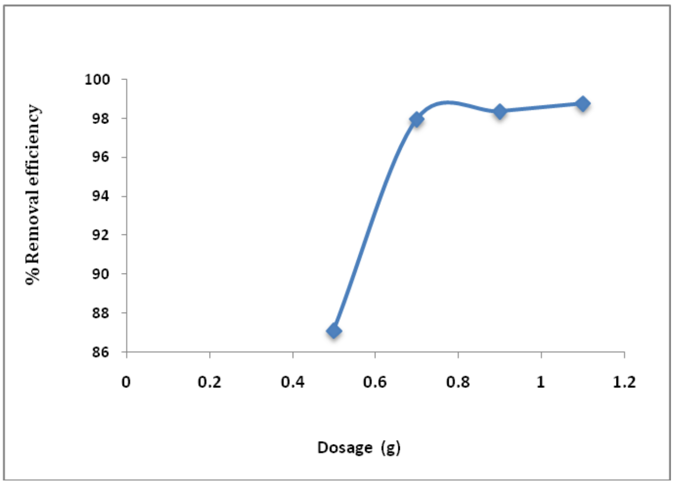

Figure -3: Effect of adsorbent dosage on Adsorption of acid yellow 17 dye on activated rice husk

c. Effect of concentration and contact time

The effect of concentration on the adsorption of acid yellow 17 dye solution was checked by varying dye concentration from 20 ppm to 100 ppm. The contact time for the adsorption of dye was also varied from the 20 to 80 minutes. The pH was maintained at 2 and the dosage of adsorbent was taken at constant value of 0.7 grams. From the Fig 4 it was observed that as the concentration was increased the adsorption was decreased. It is also observed that as contact time was increased the percentage adsorption was also increased. From the fig 4, the equilibrium contact time was found to be 80 minutes.

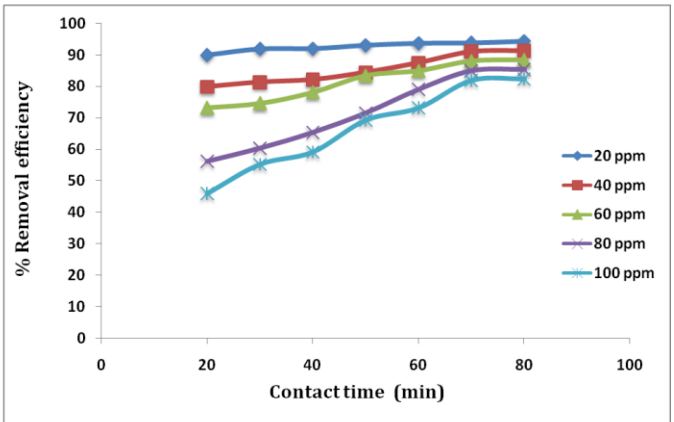

Figure 4: Effect of concentration and contact time for the removal of Acid yellow 17 on activated rice husk

d. Effect of temperature

The effect of concentration on the adsorption of acid yellow 17 dye solution was maintained at a concentration of 20 ppm, 30 ppm, 40 ppm in different conical flasks. The contact time for the adsorption of dye was maintained at 80 minutes. The pH was maintained at 2 and the dosage of adsorbent was taken at constant value of 0.7 grams in all the conical flasks. From figure 5 it was observed that increasing temperature was increased the adsorption capacity.

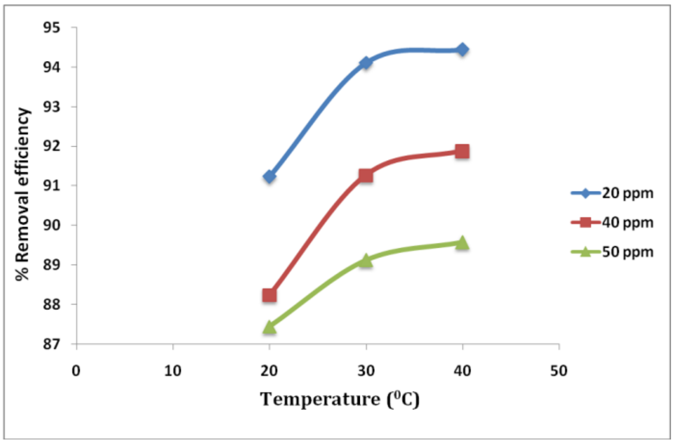

Figure -5: Effect of temperature for the removal of Acid yellow 17 using activated rice husk

e. Adsorption isotherm

Here Langmuir and freundlich isotherms are the most common isotherms to describe the adsorption isotherms

i. Langmuir adsorption isotherm

Langmuir isotherm equation is given by equation 1.

$$q_e = \frac{Q_0 b C_e}{1+bC_e} \qquad (1)$$

The linearized Langmuir isotherm is as shown in equation 2.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{C_e Q_0} \qquad (2)$$

Where C_e is the adsorbate bulk solution concentration at equilibrium (mg/L), q_e is the quantity of dye adsorbed on unit mass of adsorbent (mg/g), Q_0 is the monolayer adsorbent capacity (mg/g) and b is the constant of Langmuir adsorption isotherm (L/mg).

Langmuir isotherm is shown in the graph. In the graph the values of of $1/q_e$ vs $1/C_e$ shows a straight line with slope $(1/Q_0)$ and intercept $(1/Q_0{*}b)$. The results from the figure 6 and table 1 shows that Langmuir isotherm is good for the present adsorption study.

Table- 1: Results of Langmuir isotherm on adsorption of acid yellow 17 using activated rice husk

Langmuir isotherm	
Q_0	12.98 mg/g
b	0.2286
R^2	0.992

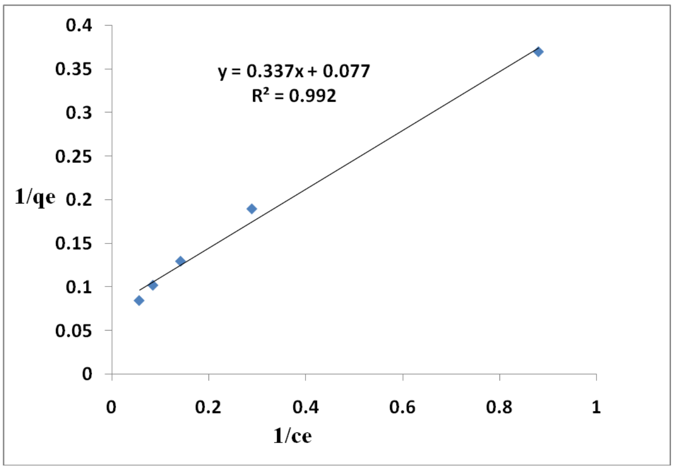

Figure- 6: Langmuir isotherm for the removal of Acid yellow 17 using activated rice husk

ii. Freundlich isotherm

Langmuir isotherm equation is given by equation 3.

$$q_e = kC_e^{\frac{1}{n}} \qquad (3)$$

Linearized form of freundlich isotherm is as shown below in equation 4.

$$\ln q_e = \ln k + \frac{\ln C_e}{n} \qquad (4)$$

Where k is the Capacity of sorption (mg/g) and n is Empirical parameter and it denotes intensity of adsorption. The smaller values of n (1 < n < 10) indicates the higher adsorption intensity. The higher value of k shows that greater amount of adsorption of adsorbate on adsorbent.

Freundlich isotherm was shown in the graph. In the graph the values of ln q_e against ln Ce shows a straight line with slope (1/n) and intercept (ln k). The results are given in figure 7 and table 2.

Table- 2: Results of Freundlich isotherm on adsorption of acid yellow 17 using activated rice husk

Freundlich isotherm	
k	2.57 mg/g
n	1.85
R^2	0.996

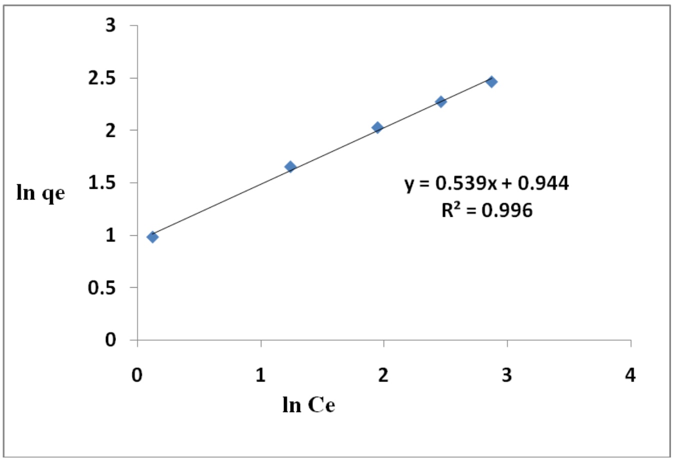

Figure- 7: Freundlich isotherm for the removal of Acid yellow 17 using activated rice husk

On comparison of Langmuir isotherm and Freundlich isotherms it was found that the adsorption studies was followed Freundlich isotherm. But the R^2 values of both isotherms were fit for present adsorption study. Figure 7 shows that the coefficient of regression for the Freundlich isotherms was 0.996 and it was higher than the Langmuir isotherm ie 0.992.

f. Adsorption Kinetics

In this study first order kinetics and second order kinetics were carried out.

i. First order kinetics

The experimental data of adsorption were used for the analysis of first order kinetics and second order kinetics. It was calculated for adsorbent dose and concentration. The first order kinetics of adsorption is given by the equation 5.

$$dq/dt = K_1(q_e - q) \qquad (5)$$

Where, q (mg/g) is the quantity of adsorbate material adsorbed at time t, q_e is the equilibrium capacity of adsorption in (mg/g) and K_1 is the first-order rate constant.

The linearized equation of equation 5 is as below.

$$\log(q_e - q) = \log(q_e) - \left(\frac{K_1}{2.303}\right)t \qquad (6)$$

A graph of log (q_e – q) against time was plotted. The straight line in the graph was showed the applicability of first order model. First order kinetics was shown in the graph 8. In the graph the values of log (q_e –q) against time was showed a straight line with slope –(K_1/2.303) and intercept (log q_e). The results are shown in table 3 and figure 8.

Table- 3: Results of first order kinetics on adsorption of acid yellow 17 using activated rice husk

First order kinetics	
K_1	0.0648
R^2	0.8058

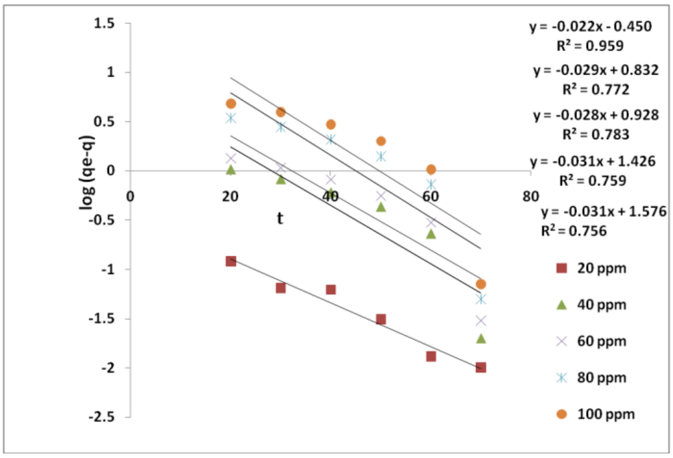

Figure- 8: First order kinetics for the removal of Acid yellow 17 using activated rice husk

ii. Second order kinetics

The experimental data of adsorption was used for the analysis second order kinetics. It was calculated for adsorbent dose and concentration. The second order kinetics of adsorption is given by the equation (7).

$$\frac{dq}{dt} = K_2(q_e - q)^2 \qquad (7)$$

Where K_2 = Second order adsorption rate constant (g/mg.min). The second order kinetics equation (7) is linearized as below.

$$\frac{t}{q} = \frac{1}{q_e{}^2K_2} + \frac{t}{q_e} \qquad (8)$$

A graph of t/q against time was plotted. The straight line in the graph shows the applicability of second order model. The intercept and slope of the graph gives the values of q_e and K_2. Second order kinetics is shown in the graph. In the graph the values of t/q against time shows a straight line with slope ($1/q_e$) and intercept ($1/q_e^2K_2$). The results are given in figure 9 and table 4.

Table- 4: Results of second order kinetics on adsorption of acid yellow 17 using activated rice husk

Second order kinetics	
K_2	0.026
R^2	0.9956

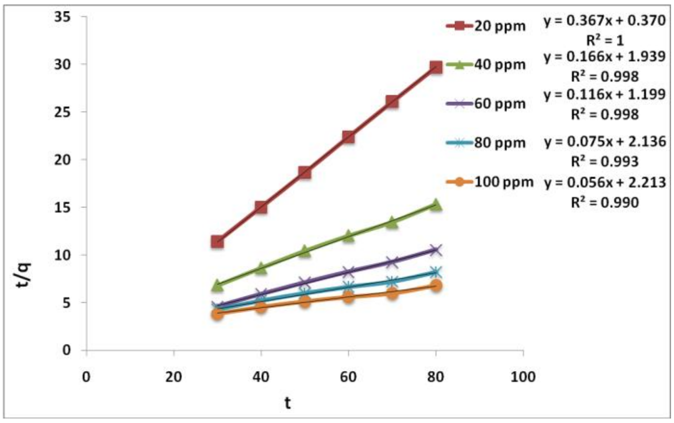

Figure- 9: Second order kinetics for the removal of Acid yellow 17 using activated rice husk

3. Conclusion

The adsorption studies for the removal of acid yellow 17 dye was carried out using activated rice husk. In this study batch adsorption studies were carried out. Effects of various parameters such as pH, adsorbent dosage, contact time, temperature and dye concentrations were investigated. The efficiency of adsorption was decreased for the increased range of concentration of acid yellow solution. Equilibrium contact time was found to be 80 minutes. The activated rice husk was adsorbed acid yellow 17 dye at a adsorption capacity of 12.98 mg/g (Q_0). The Freundlich isotherm was found to be fit for the present adsorption studies (R^2=0.996). The adsorption kinetic studies followed second order kinetics model (k=0.026).

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