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Adsorption Studies of Congo Red from Aqueous Solution on to Rice Husk.

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ABSTRACT

Adsorption is of significant importance for the effluent treatment, especially for the treatment of colored effluent generated from the dyeing and bleaching industries. Low cost adsorbents have gained attention over the decades as a means of achieving very high removal efficiencies to meet discharge standards. The present paper reports on batch investigations for color removal from aqueous solutions of Congo red (CR) using Rice Husk (RH) as an alternative low cost adsorbent. The performance analysis was carried out as function of various operating parameters, such as initial concentration of dye, adsorbent dose, contact time, particle size of adsorbent and P^H. Performance studies revealed that a very high percentage removal of color was achievable. Detailed data analysis indicated that the adsorption of CR followed Freundlich isotherm and Langmuir isotherm.

Keywords: Rice Husk; Congo red; Adsorption; Waste material

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INTRODUCTION

The effluents from textile, leather, food processing, dyeing, cosmetics, paper and dye manufacturing industries are important sources of dye pollution [1]. Many dyes and their breakdown products may be toxic for living organisms [2]. Therefore, decolorization of dyes is important aspect of wastewater treatment before discharge. It is difficult to remove the dyes from the effluent, because dyes are not easily degradable and are generally not removed from wastewater by conventional wastewater systems [3]. Generally, biological aerobic wastewater systems are not successful for decolorization of majority of dyes. Therefore, in order to achieve the desired degree of treatment, it is necessary to integrate biological, chemical and physical processes as coagulation, ultra-filtration, electro-chemical adsorption and photo-oxidation [4]. Adsorption techniques have potential for removing organics from water due to their high efficiency and ability to separate a wide range of chemical compounds [5,6]. Activated carbon has been widely used as an adsorbent in wastewater treatment to remove organic and inorganic pollutants [7–14]. Possessing high specific surface area, activated carbon frequently exhibits high removal efficiency for most dissolved compounds. It has a good capacity for the adsorption of many organic molecules. In spite of this it suffers from few disadvantages. Activated carbon is quite expensive, and its regeneration produces additional effluent and results in considerable loss (10–15%) of the adsorbent. Thus, the use of several low cost adsorbents has been studied by many researchers. They have studied the feasibility of using low cost materials, such as waste orange peel [15], banana pith [16], cotton waste, Peat, steel plant slag, fly ash and betonite clay [17], neem leaf powder [18], powdered activated sludge, perlite [19], bamboo dust, coconut shell, groundnut shell, rice husk, and straw, duck weed [20], sewage sludge [21], sawdust carbon [22] and gram husk [23] as adsorbents for removal of various dyes from wastewater. The object of the present investigations has been to evaluate the efficiency of removal of congo red using Rice Husk (RH). The performance analysis was carried out as function of various operating parameters, such as initial concentration of dye, adsorbent dose, pH, particle mesh size, and contact time. Detailed data analysis indicated that the adsorption of congo red followed Freundlich isotherm and Langmuir isotherm.

MATERIALS AND METHODS

Preparation of Adsorbent Rice Husk

Adsorbent Rice Husk was collected from rice mills. Rice hulls are the coating for the seeds or grains of the rice plant. To protect the seed during the growing season, the hull is made of hard materials, including opaline silica and lignin. The hull is mostly indigestible to humans. During the milling process, the hulls are removed from the grain to create brown rice, the brown rice is then milled further to remove the brown layer to become white rice. The very high content in amorphous silica of the hulls confer to them and to their ash (SiO_2 ~ 20 wt. %) after combustion very valuable properties. Rice Hulls contains in large percentage of amorphous silica and its combustion product (ash) is also valuable. At first Rice Husk was washed thoroughly with distilled water. Further it was treated with sodium hydroxide for about 10hours and washed with distilled water for 2 to 3 times. Further it was treated with sulphuric acid for about 4-5 hours and washed with distilled water and dried at 60^0c for 1 hour in oven. The finally obtained particles of Rice Husk were stored in air tight bottles until required.

Preparation of Congo red Solution

Stock solution of Congo red concentration was prepared by dissolving 1 gram of Congo red powder per liter of distilled water .The stock solution was then appropriately diluted to get the test solution of desired Congo red concentration varied between 0.01 to 0.03 g/l.

BATCH ADSORPTION STUDIES

Effect of Contact Time

To study the effect of contact time 0.5 grams of 14 mesh size adsorbent is taken in 50ml of aqueous solution of initial Congo red concentration 0.01 g/l ,at a known pH 6.9 and the shaking was provided for 180 minutes. The experiment was repeated for different time intervals like 15, 30, 45,…….,… 205 minutes at constant agitation speed 200 rpm, after each interval of time the sample was filtered and was analyzed for determination of optimum contact time.

Effect of Initial Concentration

To study the effect of Congo red concentration 0.5 grams of adsorbent is added to 50 ml of stock solution of Congo red concentration 0.01g/l and is kept for shaking for optimum time then the procedure is repeated at pH 6.9 with 50 ml of stock solution with different initial concentrations 0.01, 0.015, 0.02, 0.025, 0.03 g/l keeping the agitation speed and room temperature constant then the samples were filtered from adsorbent and they are analyzed for Congo red concentration.

Effect of Particle mesh Size

To study the effect of particle mesh size 50ml of 0.01g/l stock solution was added to 0.5 gram of a known particle mesh size of adsorbent i.e. 14 BSS; and it was kept for shaking for the optimum time. The sample was filtered and analyzed for concentration of Congo red. This experiment was repeated at constant agitation speed of 200rpm and room temperature with different particle sizes of adsorbent from 14-60 μm.

Effect of Adsorbent Dose

The effect of adsorbent dosage on the amount of Congo red adsorbed was obtained by agitating 50ml of Congo red solution of 0.01 g/l separately with 0.5, 1, 1.5, 2 and 2.5 grams of adsorbent at room temperature for optimum shaking time at constant agitation speed, maintaining the pH 6.9. The filtered solution of Congo red was analyzed with the help of Calorimeter.

Effect of pH

To determine the effect of pH the stock solutions of concentration 0.01g/L with 6.9 pH acid was added in order to reduce the pH value to 2, 4, 6 and base was added to increase the pH up to 10. The acid used was freshly prepared sulfuric acid and base was Sodium Hydroxide. After setting the pH of the ranges 2, 4, 6, 8 and 10 in different flasks, 50ml stock solution was pipette out and 0.5g rice husk was added into each flask and allowed to undergo shaking for 180 min. Further it was analyzed by calorimeter.

Adsorption Isotherms

The adsorption isotherms indicate distribution of adsorption molecules between the liquid phase and solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model used for design purpose. Adsorption isotherm study is carried out on two well-known isotherms, Langmuir and Freundlich. The application of the isotherm equation is compared by judging the correlation coefficients R^2. Isotherms are calculated under existing conditions. These isotherms are useful for estimating the total amount of adsorbent needed to adsorb a required amount of adsorbate from solution.

RESULTS AND DISCUSSION

Effect of Contact Time

Effect of contact time on percentage adsorption of Congo red on to Rice Husk was studied over an agitation speed of 200 rpm using 0.5grams of Rice Husk ,50ml of 0.01 g/l of individual Congo red solution concentration at pH 6.9, temperature 30^0C. The study had shown that the percentage of dye removal was high (58%). The adsorption data for the uptake of Congo red versus contact time at initial concentration 0.01g/L was shown in the Fig 1.It indicated that the adsorption of Congo red increases with increase in contact time and 180 minutes was sufficient to achieve equilibrium, with further increase the time adsorption does not occurred significantly. The amount of dye uptake was found to occur in the first rapid phase (180 min) and thereafter the sorption rate was found to be constant. This is due to more number of vacant sites are available at the initial stage and after a lapse of time, the vacant surface sites are difficult to be occupied by adsorbent molecules. This is due to repulsive forces between the adsorbent molecules on the solid and bulk phases.

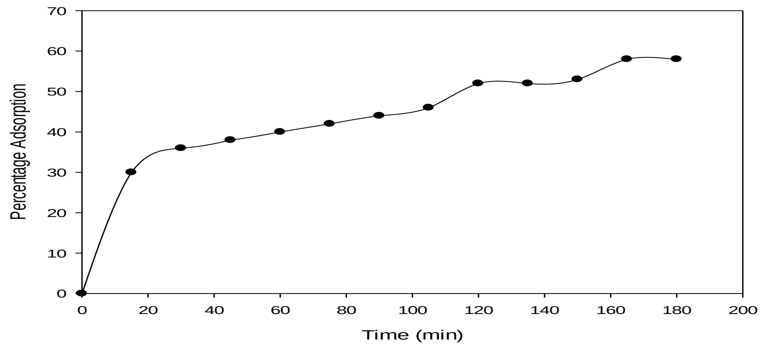

Figure 1: Effect of Contact Time on Adsorption of Congo red on to Rice Husk

Effect of Initial Concentration

The study has shown that for the Rice husk the maximum percentage of dye removal was 58% at initial concentration 0.01g/L with contact time 180min. Effect of initial concentration of dye on percentage adsorption studies is shown in fig 2. From fig 2, at initial concentration of 0.03g/L the maximum percentage of dye removal was only 43.3%. This indicates that an increase in the dye concentration decreases the percentage of dye removal, even though the amount of dye being adsorbed is increases. This is due to increase in the driving force of the concentration gradient as an increase in the initial dye concentration and the decrease in % adsorption may be attributed to lack of sufficient surface area to accommodate much more adsorbate available in the solution.

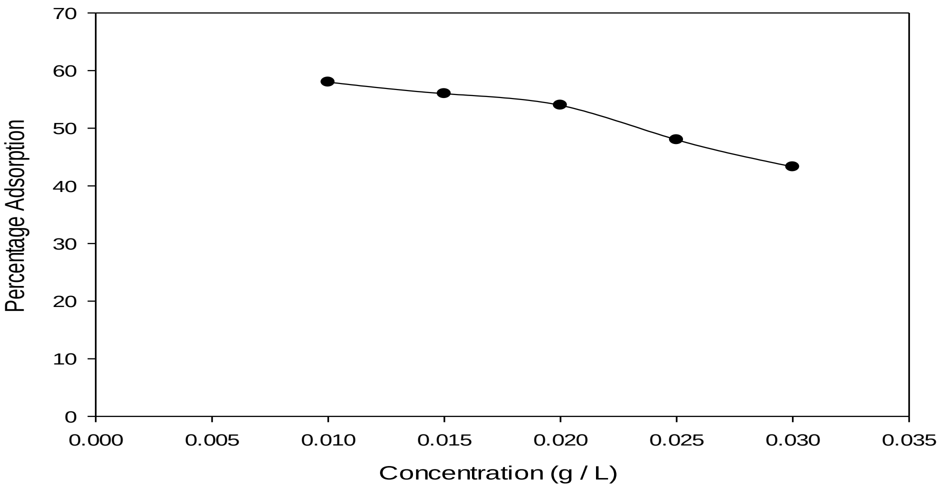

Figure 2: Effect of Concentration on Adsorption of Congo red on to Rice Husk

At lower concentrations almost all the adsorbate present in the solution could interact with the binding sites and thus % adsorption was higher than those higher at initial concentrations. At higher concentrations, lower adsorption sites yield is due to the saturation of adsorption of sites.

Effect of Particle mesh Size

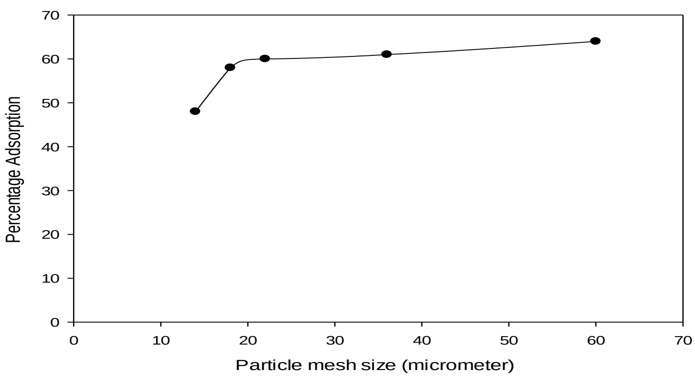

Figure 3: Effect of Particle mesh size on Adsorption of Congo red on to Rice Husk

The variation of the percentage of dye adsorption with different particle size of adsorbent is another factor influencing the percentage of dye adsorption. The present work was carried out at particle sizes <14, (14-18), (18-22), (22-36), (36-60) BSS mesh sizes and the adsorption of the dye were monitored. Effect of Particle mesh size on percentage adsorption is shown in figure 3. This indicates that as the particle size increases percentage of dye adsorption decreases and maximum adsorption about 64% can be achieved at a particle size of 36-60 BSS mesh. High percentage of adsorption with the smaller particle size occurs due to availability of more specific surface area on the adsorbent.

Effect of Adsorbent Dose

Effect of adsorbent dosage on percentage adsorption is shown in figure 4. From graph observed that the amount of the dye adsorbed varied with varying adsorbent mass. The optical density decreased from 0.75 to 0.51 for an increase in adsorbent mass from 0.5 to 2.5g, whereas percentage color removal increased from 58 % to 86 % with an increase in adsorbent mass from 0.5 to 2.5g. The decrease in optical density with increasing adsorbent mass is due to the split in the flux or the concentration gradient between solute concentration in the solution and the solute concentration in the surface of the adsorbent. The percentage of dye removal is increased due to increase in the surface area and availability of adsorption sites as adsorbent dosage increased.

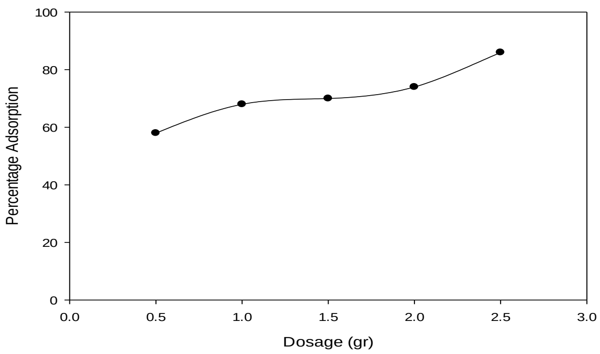

Figure 4: Effect of Adsorbent Dose on Adsorption of Congo red on to Rice Husk

Effect of pH

The effect of pH on the percentage of the Congo red is shown in figure 5 under various other fixed operating conditions. The initial pH of adsorption medium is one of the most important parameters affecting the adsorption process. It can be seen here that the percentage of dye removal was increased from 42 to 56 with an increase in the pH from 2 to 7, but there observed a decrease in dye removal from 56 to 50 for the pH 7 to 10. The adsorbent surface acidity and basicity are strong functions of pH solutions. In this case the adsorbent surface acidity might be responsible for such behavior in adsorption and such surface properties can be expressed by the following equations;

$$\text{Adsorbent-OH} \longrightarrow \text{Adsorbent-O}^- + H^+ \quad \text{(i)}$$
$$\text{Adsorbent-O}^- + H^+ \longrightarrow \text{Adsorbent-OH}_2^+ \quad \text{(ii)}$$

Equation (i) represents adsorbent surface basicity at higher pH. While Eq. (ii) represents adsorbent surface acidity at lower pH. Congo red being an anionic dye, adsorbed onto the adsorbent surface effectively at lower pH values since the adsorbent surface attained at lower pH as per Eq. (ii). As a result adsorption of Congo red on rice husk was better at pH 6-7.

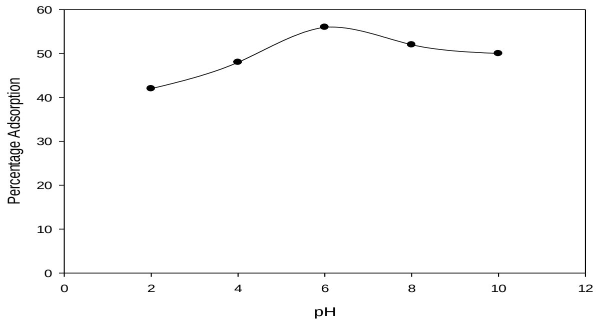

Figure 5: Effect of pH on Adsorption of Congo red on to Rice Husk

LANGMUIR ISOTHERM

Langmuir isotherms assume monolayer adsorption onto a surface containing finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface. The linear form of Langmuir isotherm equation is given as;

$$\frac{C_e}{q_e} = \frac{1}{q_0}(C_e) + \frac{1}{q_0 b} \qquad \text{(iii)}$$

Where q_o and b are Langmuir constants related to adsorption capacity and rate of adsorption respectively. A plot of (Ce/q_e) versus (C_e) for Congo red adsorption onto Rice husk is presented in the figure 6. The Langmuir constants b and q_e are obtained from the graph. The R^2 value of 0.971 indicated that the adsorption data of Congo red onto Rice husk best fitted the Langmuir isotherm model.

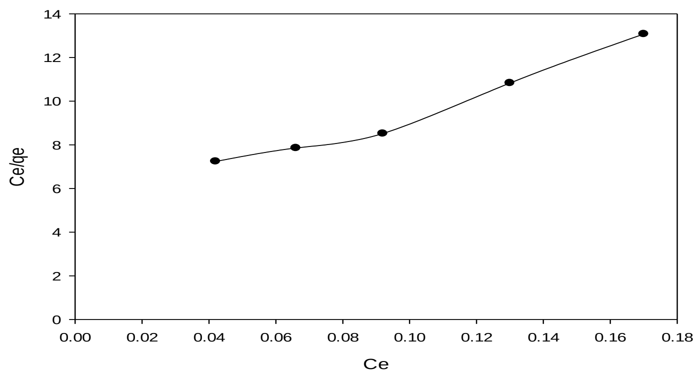

Figure 6: Langmuir adsorption isotherm at 0.5g/50ml of Adsorbate concentration

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FREUNDLICH ISOTHERM

Freundlich isotherm assumes heterogeneous surface energies but in Langmuir equation varies as a function of the surface coverage, the linearized form of Freundlich isotherm can be written as:

$$\log q_e = \log K_f + n \log C_e \qquad \text{(iv)}$$

Where K_f and n are Freundlich constants. K_f can be defined as the adsorption or distribution coefficient and represents the quality of dye adsorbed onto Rice husk for unit equilibrium concentration. The slope n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity becoming more heterogeneous as its value coming closer to zero. From the figure 7, it shows the regression value is R^2=0.947.

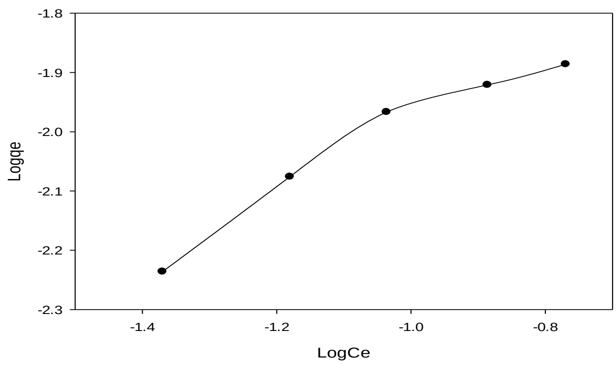

Figure 7: Freundlich adsorption isotherm at 0.5g/50ml of adsorbent concentration

CONCLUSIONS

The experimental results were analytically discussed and the following conclusions could be drawn from the study of color removal from solution of Congo red using adsorption technique.

1. The data obtained from the adsorption of Congo red on to Rice Husk showed that a contact time of 180 minutes was sufficient to achieve equilibrium.
2. It was observed that the adsorption of the Congo red decreases with increase in the initial concentration of the aqueous solution.
3. It was observed that percentage adsorption decreases with increasing particle mesh size of Rice husk.
4. The amount of adsorbate adsorbed increases with the increase of adsorbent.
5. The experimental data given good fit with Langmuir isotherm and the adsorption coefficient agreed well with conditions of favorable adsorption.

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