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Removal of Congo Red Dye from Aqueous Solutions using Steam Activated Pigmented Rice Husk Carbon as an Adsorbent: A Thermodynamic Study*

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Abstract: Dyes are very hazardous pollutant discharged in the environment in the effluents of textile industries during dyeing and rinsing processes causing detrimental effects on the workers. It is therefore fundamental to remove the dyes by using various techniques. In the present paper adsorption technique was employed for removal of Congo red dye. Congo red dye is a carcinogenic dye, which comes in the effluents of textile industries during dyeing and rinsing processes. In the present work, thermodynamic study of adsorption of Congo red dye on to steam activated pigmented carbon prepared from rice husk (B.N. ORYZA SATIVA) was investigated The adsorbent was investigated under variable system parameters, such as temperature. The results of the present study have indicated the value of ΔH were in the range of = -14.18 to -14.36 k J mol^{-1}. This suggests the adsorption of Congo red dye on SAPRHC as an exothermic process.

The (ΔS) values were in the range -47.77 to -53.91 $Jmol^{-1}K^{-1}$, which is attributed to the higher degree of ordering of the small number of the dye molecules on the solid phase compared to their ordering in the aqueous phase. The adsorbent–dye interactions are spontaneous in all the cases supported by decrease in Gibbs energy.The results obtained indicate a potential use of SAPRHC for removing dyes like Congo red dye from water.

Key words: Steam activated pigmented rice husk carbon, Congo red dye, adsorption, adsorbent, colour, exothermic.

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1. Introduction

Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications[1]. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances.

Rice husk is a byproduct of rice milling industry, accounts for about 20% of the whole rice grain. The amount of rice husk was approximately 5000 million tons in developing countries (Food and Agriculture Organization, 1995). Only 100 million tons were available annually for utilization. The amount of rice husk available is in large excess than the amounts required for any local use and thus pose disposal problems. Rice husk possesses a granular structure, is insoluble in water, and has chemical stability and high mechanical strength. Rice husk, an agricultural waste has been reported as good sorbent for many metals and basic dyes[2-4].

The adsorption capacity of rice husk very much depends on the surface activities – in other words, specific surface area available for suitable solute – surface interactions, which is accessible to the solute. In other words small particle size increases the adsorption capacity. Adsorption capacity of rice husk carbon depends not only on particle size but on activation conditions. Precalcination time has a great effect on the porosity of the porous carbons prepared from the rice husk. Lower precalcination time can produce carbons exhibiting macro porosity and meso porosity. Micro porous carbon can be produced with higher precalcination times.

Numerous approaches have been studied for the development of cheaper and effective adsorbent from rice husk. Cost and efficiency of adsorbent is actually an important parameter for comparing the adsorbent prepared[5].

2. Materials

Congo red dye used as adsorbate (purchased from S.D. Fine Chem) was used, without further purification, in the experiment. All the chemicals used were of analytical grade.

Silver nitrate was purchased from Qualigen Chemicals used to pigment carbon. Double distilled water was purchased from Loba Chemicals. The study employed steam activated pigmented rice husk carbon (SAPRHC) as an adsorbent. It was prepared from rice husk an agricultural residue obtained from Calicut, Kerala, India.

The chemical structure of dye is shown in Figure 1 and its general characteristics are indicated in Table 1.

Table 1: General characteristics of Congo red dye

Dye	Type	Form	Colour	Molecular wt. (g/mol)	Maximum wavelength of absorbance λ_{max} (nm)
Congo red	Anionic	powder	reddish brown	696.66	498

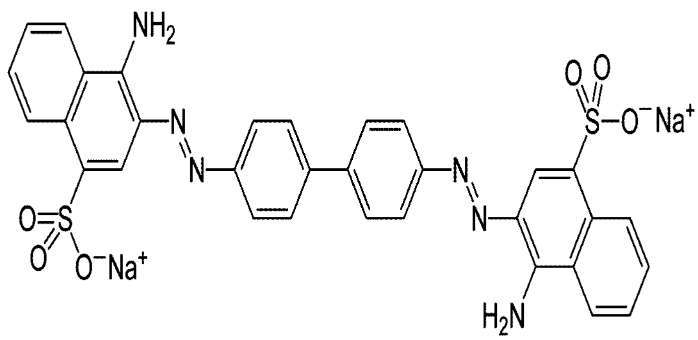

Figure 1: Chemical structure of Congo red

IUPAC Name – Sodium benzidinediazo-bis-1-naphthylamine-4-sulfonate

It is a secondary diazo dye. Congo red is the sodium salt of benzidinediazo-bis-1-naphthylamine-4-sulfonic acid. Its molecular formula: $C_{32}H_{22}N_6Na_2O_6S_2$: molecular weight: 696.66 g/mol. Congo red is a water soluble dye, yields a red colloidal solution. Its solubility is better in organic solvents such as ethanol. It has a strong, though apparently non-covalent affinity to cellulose fibers. However, the use of Congo red in the cellulose industries (cotton textile, wood pulp & paper) has long been abandoned, primarily because of its tendency to change colour when touched by sweaty fingers.

3. Parameters to be Studied

Adsorption is not an independent process it varies with many parameters, out of which temperature was studied:

- Temperature

3.1 Effect of temperature (Thermodynamics of adsorption)

Adsorption is usually an exothermic process and as the temperature increases, the amount adsorbed at a given concentration decreases in accordance with Le Chatelier's principle[9]. The thermodynamic criteria of the adsorption process were evaluated through computation of Gibbs energy (ΔG), enthalpy of adsorption (ΔH) and entropy of adsorption (ΔS) by carrying out the adsorption experiments at three different temperatures and using the following equations:

$$(\Delta G) = (\Delta H) - T\,(\Delta S), \tag{3.1}$$

$$\log (q_e / C_e) = (\Delta H) / 2.303\,RT + (\Delta S) / 2.303R\,, \tag{3.2}$$

where (q_e/C_e) is called the adsorption affinity, where q_e is the amount adsorbed per unit mass at equilibrium and C_e is the equilibrium concentration of the adsorbate. The values of (ΔH) are calculated from the slope and values of (ΔS) are determined from the intercept of the plots of $\log (q_e/C_e)$ *vs*. 1/T.

4. Methodology

4.1 Preparation of aqueous dye solutions

Solutions of Congo red dye were made from a stock solution containing 1000 mg of the dye in one liter, which was made by dissolving the required amount of dye in double distilled water. The aqueous solution of the dye had a pH of 6.9.

A number of standard solutions were made from the stock solution in the concentration range 5 ppm to 50 ppm and a calibration curve was drawn by measuring the absorbance at λ_{max} = 498 nm using the instrument, Vis scan 167. The experimental data show a straight line with a high determination coefficient (R^2 = 1.0).

4.2 Preparation of steam activated pigmented rice husk carbon as an adsorbent

Rice husk carbon was procured from Kerala and after repeated washings with double distilled water it was dried in oven at 473 K and subsequently grinded in a round ball mill (G.S.I. Lab, Faridabad, India) to a mesh size of 40 to 60 µm. This powdered carbon was activated by steam in a specially designed vessel for 3 to 4 hour. After that, 1% $AgNO_3$ solution was added and it was kept in sunlight for pigmentation. Heating of pigmented carbon was done in an oven for 7 to 8 hour at 653 K (in vacuum) and stored in air tight container in desiccators in presence of KOH & $CaCl_2$.

4.3 Adsorption experiments with steam activated pigmented rice husk carbon

All adsorption experiments were done without adjusting the pH, as the pH of the aqueous solutions of dyes does not change much with dilution. The batch adsorption was carried out in 250 mL borosil conical flasks by mixing a pre - weighed amount of the SAPRHC with 100 mL of the aqueous dye solution of a particular concentration. The conical flasks were kept on a magnetic shaker maintained at a constant temperature of 303 ± 2K (except for thermo dynamic studies) and were agitated for a pre-determined time interval at a constant speed.

The system parameters such as intra particle diffusion and temperature of adsorption were controlled during the experiments. After adsorption was over, 5 mL solution was taken out by means of syringe and centrifuged for 15 to 20 minute and the un-adsorbed remaining dye was determined spectrophotometerically.

5. Results and Discussion

5.1 Thermodynamic studies

In environmental engineering practice, both energy & entropy consideration must be taken into account in order to determine what processes will occur spontaneously.

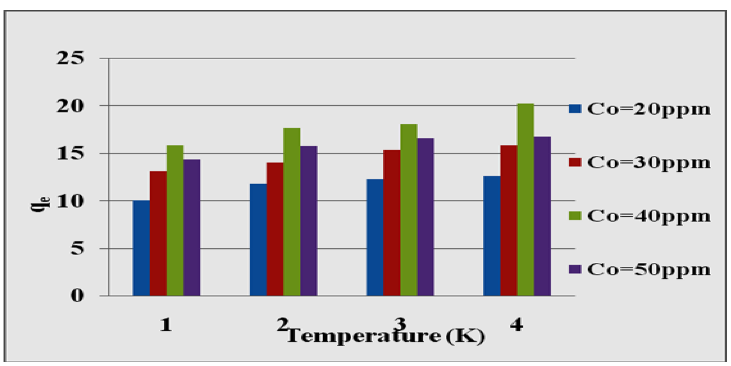

Figure 2: Variation of amount of adsorbed Congo red dye per unit mass of adsorbent with temperature

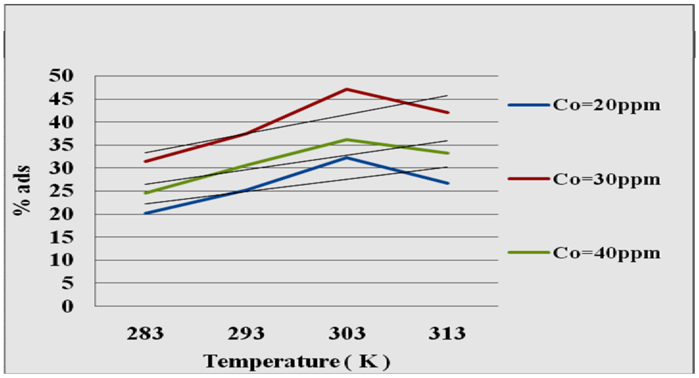

Figure 3: Variation of extent of Congo red dye adsorbed with temperature

In the present work the effect of temperature on adsorption was studied at 5 different temperatures *viz.* 288, 293, 298, 303 and 308K with a constant agitation time of 6 hours and a constant amount of SAPRHC (0.8 g/L) at 5 different concentrations of the dye. The amount of dye adsorbed per unit mass of SAPRHC showed a linear increase first and then decrease with increasing temperature (Figure 2 & 3).

The Vant's Hoff plots of log (q_e / C_e) *vs.* 1/T were linear (Figure 4) with regression coefficient R lying between 0.401 and 0.638.

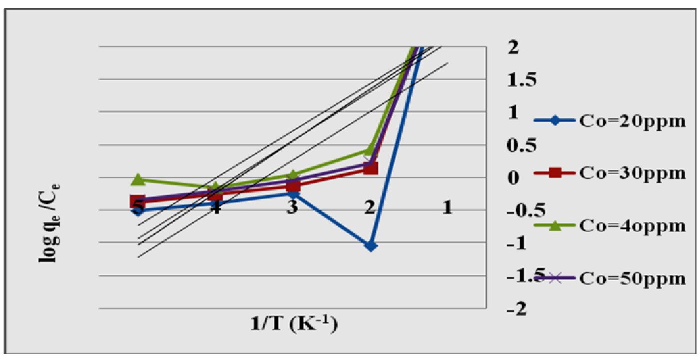

Figure 4: Variation of log q_e /C_e *vs.* 1/T (K^{-1})

The values obtained for the thermodynamic parameters from these plots for the temperature range 288 to 308 K are given in Table – 2.

The adsorption process was exothermic with heats of adsorption (ΔH) values in the range -13.82 to -15.24 kJmol $^{-1}$ mean value -14.4 kJmol^{-1} for the concentration range 10 to 50 ppm of the dye solution.

Table 2: Thermodynamic parameters (adsorbent dose 0.8 g/L)

Dye	**ΔH (k $Jmol^{-1}$)**	**ΔS (J mol^{-1} K^{-1})**
20	-4.187	-47.77
30	-15.24	-56.46
40	-13.82	-55.31
50	-14.36	-53.91
Mean	-14.4	-53.36

These values did not indicate strong chemisorptive bond formation between the dye molecules and the adsorbent surface. The ΔH values demonstrate the process to be spontaneous without requiring any energy input from outside. The process was accompanied by a decrease in entropy values. The (ΔS) values were in the range -47.77 to -53.91 $Jmol^{-1}K^{-1}$, which could be attributed to the higher degree of ordering of the small number of the dye molecules on the solid phase compared to their ordering in the aqueous phase[10].

The results of the measurement of the thermodynamic parameters indicate that the Congo red dye-SAPRHC interaction equilibrium could be explored for practical applications.

At high temperatures due to increase in the mobility of solute molecules and expansion in the pore size of the adsorbent, some of the dye molecules from the interior of the adsorbent will be released into the solution. Similar mechanism was suggested by Ho and Chiang (2001)[11] for exothermic adsorption of dyes like Acid blue-9 on a mixture of activated clay and activated carbon. Similar results have been reported by Ho & McKay (2003)[12] for different adsorbents.

6. Conclusion and Recommendations

6.1 Conclusion

A batch system was applied to study the adsorption of Congo red from water by SAPRHC adsorbent prepared from rice husk waste residue obtained from agriculture industry.

From the experimental findings in the present work, the following conclusions can be drawn:

(1) SAPRHC has shown sufficient potential as an adsorbent for the removal of Congo red dye from water. A small amount (0.8 g L^{-1}) of the adsorbent

can decolourize more than 60% of Congo red dye from aqueous solutions (10 ppm) if agitated for 300 minute.

(2) The adsorption of Congo red dye on SAPRHC was exothermic in nature accompanied by both an entropy decrease and decrease in Gibbs energy. With increase in temperature, the dye removal capacity was decreasing due to the increasing mobility of the dye molecules as well as pore expansion. The value of enthalpy change and entropy change were ΔH = - 14.4k J mol^{-1} and ΔS = 53.36 $Jmol^{-1}K^{-1}$ for Congo red dye.

(3) The adsorbent–dye interactions are spontaneous in all the cases supported by decrease in Gibbs energy.

(4) The results of the experiments showed that most of the dye adsorption took place in the first 15 to 30 minute of contact times and equilibrium reached within 300 minute for SAPRHC, at optimum dose of 0.8 g/L of the adsorbent dose.

6.2 Recommendations

The Steam Activated Pigmented Rice Husk Carbon (SAPRHC) prepared from rice husk waste residue obtained from agriculture industry can be considered as low cost adsorbent as its preparation method is very easy and economic. Furthermore, this adsorbent is abundant in nature and there is no economic aspect involved. It prevents the disposal problems and hence we need not to worry about its regeneration. Thus there is a promising scope for the large scale application of the adsorbent to remove the most problematic, water soluble dyes from textile effluents. However, much work is yet required in this area of to study the mechanism of adsorption process for dye removal from real textile effluents under a wide range of operating conditions. Moreover, better understanding of adsorption mechanism is also essential to estimate economic feasibility of SAPRHC for large scale applications. Thus, SAPRHC can truly be termed as a low-cost adsorbent.

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