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Thermodynamic Study of Adsorption of Amaranth Dye on to Steam Activated Pigmented Rice Husk Carbon

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Abstract: In the present work, thermodynamic study of adsorption of Amaranth 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 intra particle diffusion and temperature. The results of the present study have indicated the value of ΔH were in the range of -1.302 to -4.710 kJmol $^{-1}$. This suggests the adsorption of Amaranth dye on SAPRHC as an exothermic process. The (ΔS) values were in the range -9.994 to -25.140 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 Amaranth dye from water.

Keywords: Steam activated pigmented rice husk carbon, Amaranth dye, adsorption, adsorbent, colour, exothermic.

1. Introduction

Adsorption is a well-known equilibrium separation process and an effective method for water decontamination applications [1] (Dabrowski, 2001). 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] (Lee *et al*., 1999; Marshall *et al*., 1993; Suemitsu *et al*., 1986).

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. Adsorption capacity increases with a large surface area. 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.

The BET (Brunauer-Emmett-Teller) surface area, pore volume, average pore diameter of carbon depend on activation time, activation temperature and ratio of activation agents.

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] (Jain *et al*., 2003).

2. Materials

Amaranth 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 characteristic of Amaranth

Dye	Type	Form	Colour	Molecular wt. (g/mol)	Maximum wavelength of absorbance
Amaranth	anionic	powder	reddish	604.47	520

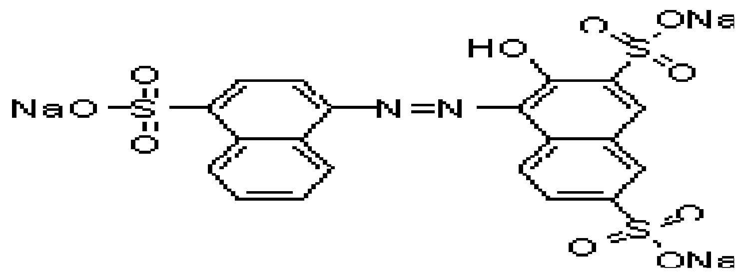

Fig.1 Chemical structure of Amaranth

IUPAC Name – Trisodium (4E) -3-oxo-4 [(4-sulfonato-1-naphthyl) hydrazono] naphthalene - 2, 7-disulfonate

It can be applied to the natural and synthetic fibers, leather paper and phenol-formaldehyde resins. Initially it was used as a food dye and to colour cosmetics, but since 1976 it has been banned to colour cosmetics.

3. Parameters to be Studied

Adsorption is not an independent process it varies with many parameters, following parameters were studied:

- Effect of Intra particle diffusion rate
- Temperature

3.1. Effect of intra - particle diffusion rate

The variation in the amount of adsorption with time at different initial concentrations of dye is further processed by evaluating the role of diffusion in the adsorption process. Adsorption is a multi-step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particulates followed by diffusion of the solute molecules into the pore interiors [6](Sivraj *et al*., 2001). The intra - particle diffusion rate is given by the equation[7-8] (Weber and Morris, 1963; Mckay et al., 1989).

(3.1) $$q_t = k_i t^{0.5},$$

where k_i is the intra-particle diffusion rate constant. The values of k_i are calculated from the slopes of q_t *vs*. $t^{0.5}$ plots.

3.2. 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] (Kadirvelu *et al*., 2003). 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:

(3.2) $$(\Delta G) = (\Delta H) - T (\Delta S),$$

(3.3) $$\log (q_e / C_e) = (\Delta H) / 2.303 RT + (\Delta S) / 2.303R,$$

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

a. Preparation of aqueous dye solutions

Solutions of Amaranth 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 7.1.

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} = 560 nm using the instrument, Vis scan 167. The experimental data show a straight line with a high determination coefficient (R^2 = 1.0).

a. Preparation of steam activated pigmented rice husk carbon as an absorbent

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 & $CaCl_2$.

b. Adsorption experiments with steam activatedpigmented 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 (fitted with filter paper) and centrifuged for 15 to 20 minute and the un-adsorbed remaining dye was determined spectrophotometerically.

5. Results and discussion

5.1. Intra-particle diffusion

An adsorption process is normally controlled by three diffusion steps (1) transport of the solute from bulk solution to the film surrounding the adsorbent, (2) transfer from the film to the adsorbent surface, leading to surface adsorption and (3) diffusion from the surface to the internal sites followed by binding of the adsorbate on the active sites. The slowest of these steps determines the overall rate of adsorption process. If intra particle diffusion has significant presence in the adsorption process [7] (Weber and Morris, 1963), the approach toward equilibrium is governed by the function $(D_t / r^2)^{0.5}$ where r is the radius of the particle and D is the diffusivity within the particle. The initial rate of the intra-particle diffusion is obtained with the help of equation (9) by plotting q_t versus $t^{0.5}$. The plots show multi linearity with two or more steps as shown in Figure 2.

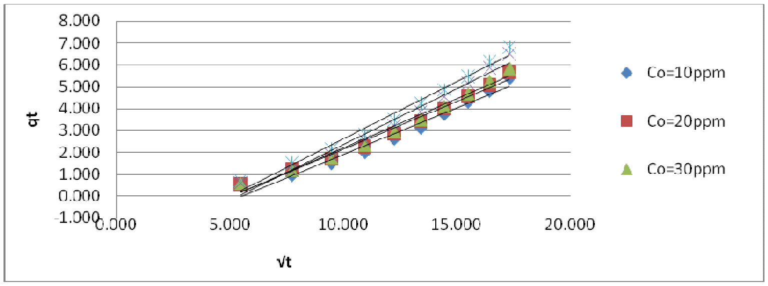

Fig.2 The q_t *vs.* $t^{0.5}$ plots (Temperature 300 K SAPRHC amount 0.8 g/L)

The plots of q_t *vs.* $t^{0.5}$ were found to yield straight lines (Figure 2) with regression coefficients 0.973 to 0.983. The intra-particle diffusion rate constant k_i was in the range of 0.425 to 0.521ppm/g $min^{0.5}$ (mean k_i=0.468 ppm/g $min^{0.5}$). The linearity of the plots showed that intra-particle diffusion might have a significant role in the adsorption of the dye (Amaranth) on the adsorbent.

5.2. Thermodynamic studies

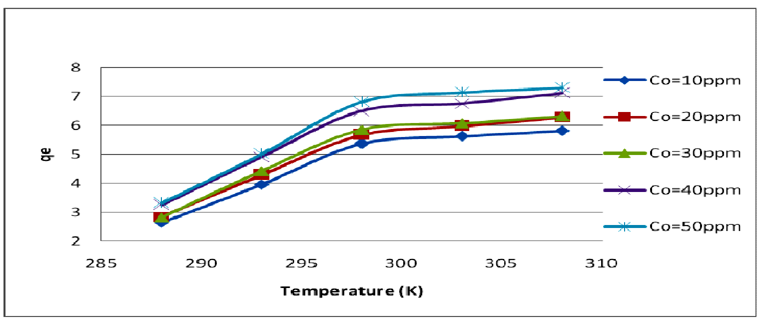

Fig.3 Variation of amount of adsorbed Amaranth dye per unit mass of adsorbent with temperature.

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

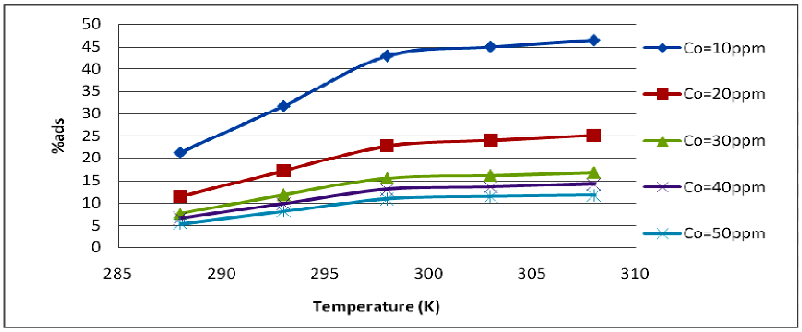

Fig. 4 Variation of extent of Amaranth dye adsorbed with temperature

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 3 &4).

The Vant's Hoff plots of log (q_e / C_e) *vs.* 1/T were linear (Figure 5) with regression coefficient R lying between 0.822 and 0.89.

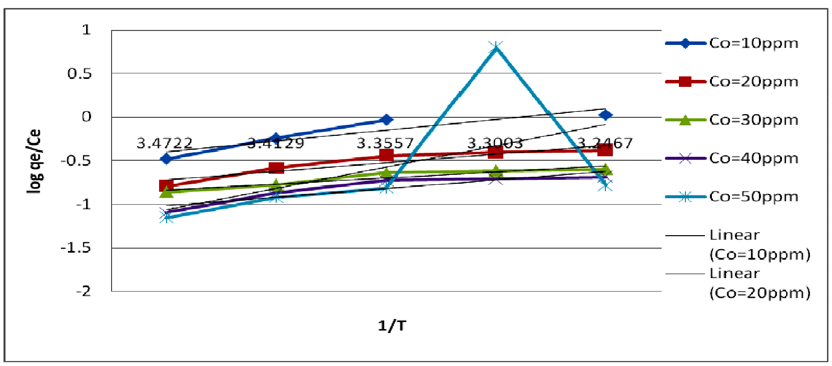

Figure 5: Variation of log q_e /C_e *vs.* 1/T (K^{-1})

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 -1.302 to -4.710 kJmol $^{-1}$ mean value -2.437 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 concentration(ppm)	**ΔH (k J mol^{-1})**	**ΔS (J mol^{-1} K^{-1})**
10	-2.355	-9.994
20	-1.947	-15.777
30	-1.3019	-17.289
40	-1.876	-21.329
50	-4.71	-25.14
mean	-2.437	-17.905

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 -9.994 to -25.140 $Jmol^{-1}K^{-1}$, 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](Ho *et al*., 2005) .

The results of the measurement of the thermodynamic parameters indicate that the Amaranth 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 Amaranth

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 Amaranth dye from water. A small amount (0.8 g L^{-1}) of the adsorbent

can decolourize as much as 43% of Amaranth dye from aqueous solutions (10 ppm) if agitated for 300 minute.

(2) The adsorption of Amaranth 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 = - 2.4k J mol^{-1} and ΔS = 17.905 $Jmol^{-1}K^{-1}$for Amaranth 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.

(5) Furthermore, intra-particle diffusion was not the only step to control adsorption of the dye. Diffusion of dye particles into the pores follows a large number of steps.

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.

References

1. A. Dabrowski, Adsorption from theory to practice. *Adv. Colloid Int. Sci.,* **93** (2001) 135-224.
2. C. K. Lee, K. S.Low, S. C.Liew and C. S. Choo, Removal of Arsenic (V) from aqueous solution by quaternized rice husk. *Environ. Technol.,* **20** (1999) 971-978.

3. W. E. Marshall, E. T., Champagne and W. J. Evans, Use of rice milling by products (hulls and bran) to remove metal ions from aqueous solution, *J. Environ. Sci., Health* (**A) 28** (1993) 1977-1992.

4. R. Suemitsu, R. Uerishe, I. Akashi and M. Nakano, The use of dyestuff-treated rice hulls for removal of heavy metals from waste water. *J. Appl. Polymer Sci.,* **I** (1986) 75-83.

5. A. K. Jain, V. K. Gupta, A. Bhatnagar and Suhas, Utilization of industrial waste products as adsorbents for the removal of dyes, *J. Hazardous Mater.,* **(B) 101** (2003) 31-42.

6. R. Sivaraj, C. Namasivayam and K. Kadirvelu, Waste management, orange peel as an adsorbent in the removal of acid violet from aqueous solution. *Waste Manag.,* **21** (2001) 105.

7. W. J. Weber and J.C. Morris,. Kinetics of adsorption on carbon from solution. J. Sanity Eng. Div. *Am. Soc. Civil Eng.* **89** (1963) 31-59.

8. G. McKay, H.S. Blair and J.R. Gardner, The adsorption of dyes onto chitin in fixed bed column and batch absorbers. *J. Appl. Polym. Sci.,* **28** (1989) 1499-1544.

9. K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani and S. Pattabhi, Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions. *Bioresour. Technol.* **87** (2003) 129-132.

10. Y. S. Ho and C. C. Chiang, Sorption studies of acid dye by mixed sorbents. *Adsorption* **7** (2001) 139-147.

11. Y. S. Ho, T. H. Chiang and Y. M. Hsueh, Removal of basic dye from aqueous solutions using tree fern as a biosorbent. *Process Biochem.* **40** (2005) 119-124.

12. Y. S. Ho and G. McKay, Sorption of dyes and copper ions onto biosorbents. *Process Biochem.* **38** (2003) 1047-1061.