RJC Rasayan J. Chem. Vol.1, No.4 (2008),936-942

A STUDY ON REMOVAL OF CONGO RED DYE FROM THE EFFLUENTS OF TEXTILE INDUSTRY USING RICE HUSK CARBON ACTIVATED BY STEAM

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ABSTRACT

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. The technique was found to be very useful and cost effective for a better removal of dye. Although commercial activated carbon is a preferred sorbent for colour removal, its wide spread use is restricted due to high cost. Currently, the study of activated rice husk carbon as a low cost sorbent for removing dye has drawn attention of various researchers working in this field. In the present work, rice husk carbon (RHCAS) in the form of powder was investigated for removing dyes taking Congo Red as a model system. The adsorbent was made from rice husk procured from Kerala and was investigated under variable system parameters such as agitation time and dose of adsorbent. An amount of 0.08 g/l of RHCAS could remove 10 to 99 % of the dye from an aqueous solution of 25 ppm with the agitation time increasing from20 min to 200 min. The interactions were tested for both pseudo first- order and second – order kinetics and it was observed that the interactions could be better explained on the basis of first order kinetics.

Keywords: *Activated carbon, adsorption, effluents, congo red, contact time, rice husk*

INTRODUCTION

Dyes are widely used in industries such as textiles, rubber, paper, plastics, cosmetics, etc., to colour their products. The dyes are invariably left as the major waste in these industries. Due to their chemical structures, dyes are resistant to fading on exposure to light, water and many chemicals and, therefore, are difficult to be decolourised once released into the aquatic environment[1-2]. Many of the organic dyes are hazardous and may affect aquatic life and even the food chain[3]. For example, congo red dye (1-Naphthalenesulfonic acid, 3, 3'-(4, 4' biphenylene bis (azo) bis 4-amino) di sodium salt) is a benzedene based dye, known to metabolize to benzedene, a known human carcinogen. Exposure to the dye has been known to cause an allergic reaction (and possibly anaphylactic shock). The removal of dyes from industrial waste before they are discharged into the water bodies is therefore very important from health and hygiene point of view and for environmental protection[4]. The need and urgency can be gauged from the fact that in developed countries such as the UK and many EU countries, environmental policies have required that zero synthetic chemicals should be released into the marine environment[5]. Various techniques have been employed for the removal of dyes from wastewaters[6-14]. Conventional physical and chemical methods are either costly, or produce concentrated sludge, or may not capable of treating large volumes of effluent without the risk of clogging[15]. Pearce and his co-workers have presented a comprehensive review of a method using bacterial cells to remove the dye from textile wastewater is given by et al. [16].

Natural materials that are available in abundance, or certain waste products from industrial or agricultural operations, may have great potential as an inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration. The abundance and availability of agricultural by-products make them good sources of raw materials for activated carbons. Many carbonaceous materials such as bark, coal, lignite, coconut shells, wood, dead biomass, seaweed, pecan shell and peat are used in the production of commercial activated carbons[17,18].

Present Work:

With the exponential demand in the use of rice as a staple food, the rice husk which is a waste product is available in abundance i.e. far in excess of any local uses and, thus, has posed disposal problems [19]. Rice husk possesses a granular structure, is insoluble in water, has chemical stability and high mechanical strength. The typical composition and chemical composition of rice husk is given elsewhere[20-22]. A previous study has reported that the rice husk has a low calorific value of 3585 kcal/kg and high ash content[23]. Due to its high ash content, a proper method of disposal and utilization of rice husk has yet to be developed[24]. The abundance of rice husk has been well documented by Grist[25]. From the statistical data of the Food and Agriculture Organization (FAO), 1995, there is an estimated annual rice production of 500 million tons in developing countries and approximately 100 million tons of rice husk is available annually for utilization in these countries alone. The rice husk, as the commodity waste, can be activated and used as an adsorbent in water purification or the treatment of industrial wastewater. It would add value to these agricultural commodities, help reduce the cost of waste disposal, and provide a potentially cheap alternative to the existing commercial carbons. Rice husk, an agricultural waste, contains about 20% silica, is suitable for the production of activated carbon and has been reported as a good sorbent for many metals and basic dyes[26-45]. The reported dye adsorption capacities (mg/g) for rice husk are different for different dyes.

In the present work, we have reported on the use of activated rice husk as a sorbent for the removal of water-soluble dyes present in wastewater.

EXPERIMENTAL

Commercially available black carbon prepared from rice husk was grinded in a round ball mill, washed several times with double distilled water and activated by high temperature steam for 4 hours then by heating in a constant temperature oven at 380^0C for 6 hours and preserved in an air tight container, before it was used as adsorbent of Congo red dye purchased from Loba chemicals. The dye Congo red (Loba chemicals) was used without further purification. A stock solution containing 1000mg of dye in 1 litre was made by dissolving the required amount of Congo red in double distilled water. The aqueous solution of the dye had a pH of 6.7. A number of standard solutions were made from the stock solution in concentration range 5 to 60 mg/l and a calibration curve was drawn by measuring the absorbance at λmax = 497nm using visible spectrophotometer, Visiscan 167 Systronics, purchased from Systronics.

The pH of the aqueous solutions of Congo red was approximately 6.7 which did not change much with dilution there fore all experiments were done without adjusting the pH. The batch adsoption was carried in 250 ml Borosil conical flasks by mixing a pre-weighed amount of the SARHC with 100 ml of aqueous dye solution of a particular concentration. The conical flasks were kept on a magnetic shaker and were agitated for a pre-determined time interval at a constant speed. The system parameter such as adsorbent amount, agitation time and temperature were controlled during the experiments. After adsorption was over, the mixture was allowed to settle for 10 min. The supernatant liquid portions were centrifuged for 20 min and the dye remaining unadsorbed was determined spectrophotometrically. The adsorption experiments were carried out in a batch process under the following conditions:

• Initial conc. of congo red solution (ppm):	25
• Amount of adsorbent (gm/l):	0.01, 0.02, 0.04, 0.06, 0.08
• PH:	6.7
• Agitation time (min.):	20, 40, 60, 80, 100, 120, 140
• Particle size (μm):	20 – 40

Amount of congo red dye adsorbed per unit mass of the adsorbent, q (mg/g) was computed by using the following equation.

$$q = (C_0 - C_t) / m \qquad (1)$$

where C_0 and C_t are congo red conc. in ppm before and after time t, and m is the amount of SARHC taken for 1 litre of Congo red solution. The extent of adsorption in % is found from the relation

$$\text{Adsorption (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (2)$$

4. Kinetics of adsorption

The mechanism of adsorption often involves chemical reaction between functional groups present on the adsorbent surface and the adsorbate, system parameters such as temperature and pH[4]. The order of adsorbate-adsorbent interactions has been described by using various kinetic models. In the present work, we have used the pseudo-first order model derived by Lagergren[49], although several authors report that the second-order kinetics can also be applied to these interactions in certain specific cases.

In the case of adsorption preceded by diffusion through a boundary, the kinetics in most cases follows pseudo- first- order equation of Lagergren:

$$dq/dt = K_{ad}(q_e - q_t) \qquad (3)$$

where q_t and q_e are the amount adsorbed at time t and at equilibrium, and K_{ad} is the rate constant of the pseudo- first-order adsorption process. The integrated rate law, after applying the initial condition of qt = 0 at t = 0, is

$$\log(q_e - q_t) = \log q_e - (K_{ad}/2.303)t \qquad (4)$$

Plot of $\log(q_e - q_t)$ versus t gives a straight line for first-order kinetics, which allows computation of the adsorption rate constant, K_{ad}. If the experimental results do not follow eqs. (3) and (4) , they differ in two important aspects; (i) $K_{ad}(q_e - q_t)$ then does not represent the no. of available sites, and (ii) $\log q_e$ is not equal to the intercepts of the plot of $\log(q_e - q_t)$ against t. In such cases, pseudo-second-order kinetics[4,11] given by-

$$dq/dt = k_{2(}q_e - q_t) \qquad (5)$$

where k is the second –order rate constant, is applicable. For the boundary conditions t = 0 to t = t and $q_t = q_t$, the integrated form of equation is

$$1/(q_e - q_{t)} = 1/q_e + k_2 t \qquad (6)$$

which can also be written as

$$q_t = 1/(1/k_2 q_e^2) + t/q_e \qquad (7)$$

or in the linear form,

$$t/q_t = 1/h + (1/q_e)t \qquad (8)$$

where $h = k_2 q_e^2$ can be regarded as the initial sorption rate as t→0. If the pseudo second order kinetics is applicable, the plot of t/q_t vs t gives a linear relationship, which allows computation of q_e, k_2 and h without having to know any parameter beforehand.

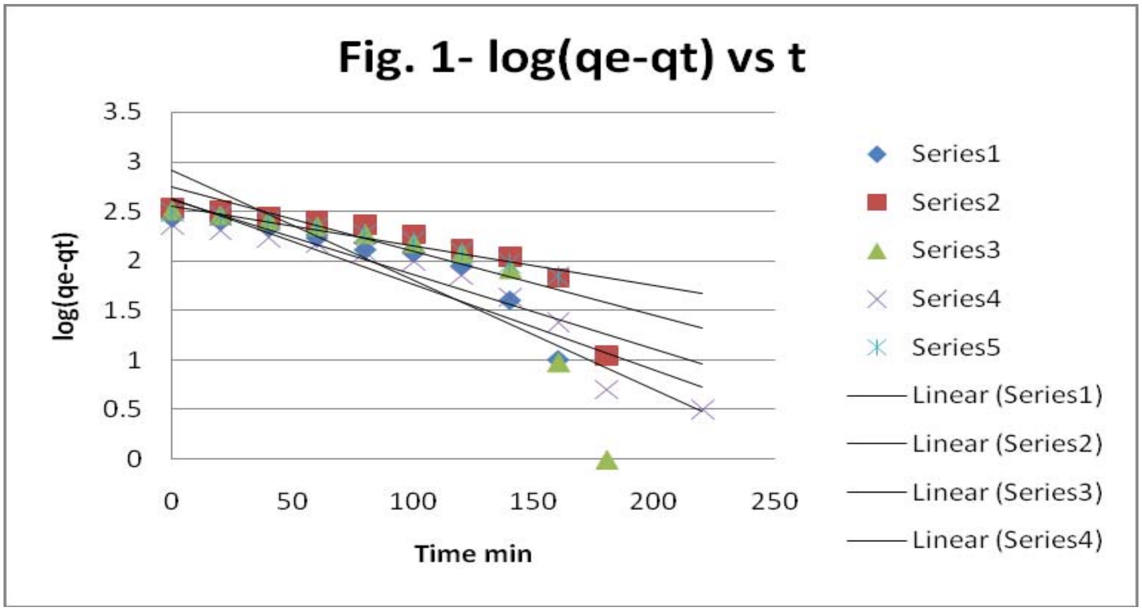
RESULTS AND DISCUSSION

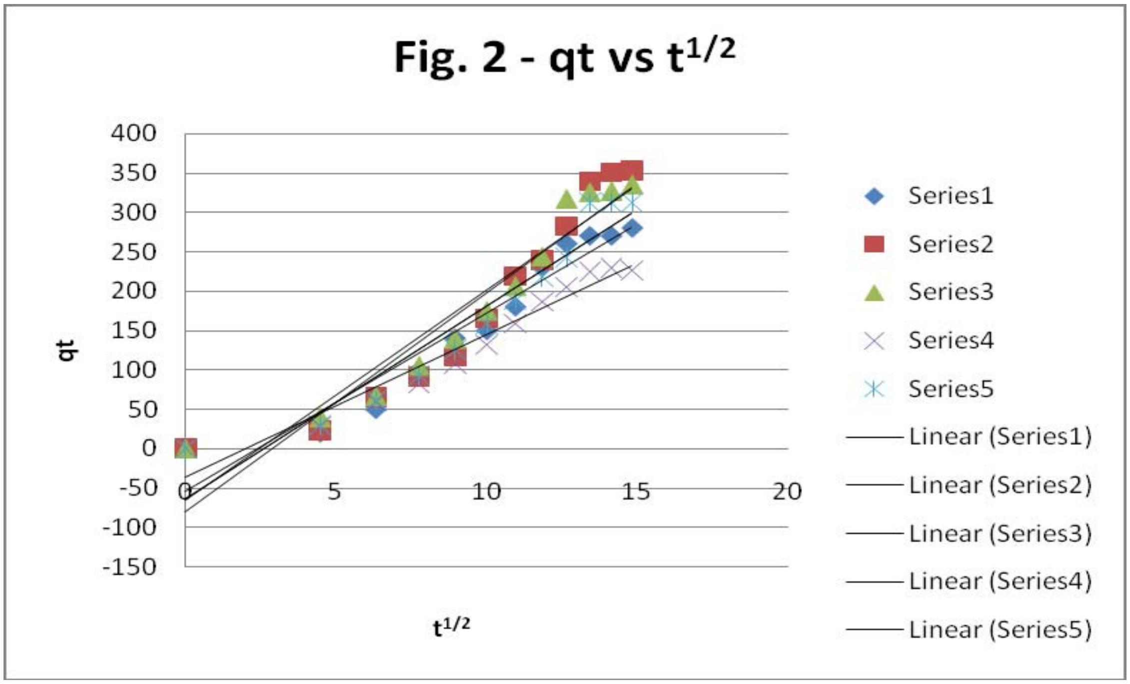
Influence of agitation time and kinetics of adsorption:

The agitation time affected the extent of adsorption of the dye. Table 1 shows the variation in the extent of adsorption (%) of congo red on SARHC at 300 K with time for constant dye concentration. When amount of steam activated rice husk carbon (SARHC) was increased from 0.01 g/l to 0.08 g/l, there was enhanced dye removal from 4.0 to 29.60 % at 60 min. agitation time with an aqueous Cong red solution of concentration 25 ppm. The corresponding increase was from 10.8 to 99.1 % at 300 min. agitation time. The plots of $\log(q_e - q_t)$ vs agitation time (t) were nearly linear as shown in fig 1. The first order rate constant, k_1 was in the range of 1.12×10^{-2} - 1.15×10^{-2} min^{-1} with an average value of 1.14×10^{-2} min^{-1}. Several authors have reported similar pseudo first order kinetics for adsorption of dyes on various adsorbents. The values of k_1 obtained in this work are comparable with those reported by earlier workers[4,54-57]. To test second-order kinetics graphs were also plotted between t/q_t and t, but due to different nature of adsorbent, results do not show second order kinetics.

Table-1: Extent of adsorption % of Congo red on SARHC at 300 K with increasing agitation time and adsorbent amount (dye concentration 25 ppm)

Agitation time (min)	Extent of adsorption (%) for SARHC amount in (g/l)				
	0.01	0.02	0.04	0.06	0.08
20	0.8	1.84	6.36	6.84	9.32
40	2.0	5.24	10.78	14.36	19.72
60	4.0	7.28	16.84	19.80	29.60
80	5.6	9.32	22.32	25.80	40.08
100	6.0	13.20	28.00	31.88	50.44
120	7.2	17.52	33.04	38.16	60.12
140	9.2	19.12	39.08	44.88	69.80
160	10.4	22.56	50.80	49.94	77.56
180	10.8	27.12	52.16	54.00	100.00
200	10.4	28.00	52.40	55.36	100.00
220	11.2	28.24	53.76	54.44	100.00





Intra particle diffusion:

The plots of q_t vs $t^{1/2}$ as shown in fig. 2 were found to yield straight lines with regression co-efficient of 0.902. The intra particle diffusion rat constant k_i was 2.77×10^{-1} m mol g^{-1} $min^{-1/2}$.The linearity of the plots showed that intra particle diffusion might have a significant role in the adsorption of the dye Congo red on SARHC. The adsorption of the dye on SARHC could not be described by simple mechanism of surface only[58], and it is likely that the adsorption on the external surface was followed by diffusion in to the pores as well as to the large number of steps and kinks on the surface. If the two steps are independent of one another, the plot of q_t vs $t^{1/2}$ appears as a combination of two or more intersecting lines[58], the first of the lines represents surface adsorption and the second intra particle diffusion. The absence of such distinctive features in the plots of the present work could be interpreted as due to very little distinction between the two steps. Surface adsorption and intra particle diffusion were likely to take place simultaneously, both processes controlling the kinetics of dye - solid interactions. The pores and the steps on the SARHC particles were such that they could accommodate the Congo red molecules[4]. It is still not easy to draw a conclusion about the rate-limiting step. Weber and morris (1963) (59) have originally proposed that if the uptake of the adsorbate varies with square root of time, intra particle diffusion can be taken as the rate-limiting step. Equation $q_t = k_i\ t^{1/2}$ requires that the q_t vs $t^{1/2}$ plots should have zero intercept if the intra-particle diffusion is the sole rate-limiting step. Since this was not the case in the present work, it is obvious that intra particle diffusion is not the dominating mechanism for the adsorption of the dye on SARHC. Similar types of results have been reported by other workers on Neem leaf powder[4].

CONCLUSION

The findings of the present work reveal that the rice husk which is easily and abundantly available agro waste in our country can be easily converted into good adsorbent by using simple methods of activation. A small amount (0.08 g/l) of the SARHC adsorbent could decolourize as much as 99% of the dye from an aqueous solution (25 ppm) if agitated for 200 min demonstrated sufficient potential of SARHC as an adsorbent for the removal of the dye Congo red, from water solutions. The adsorption of the dye was maximum around the natural pH of the aqueous solution of Congo Red. This shows that adsorption of the dye could be carried out on SARHC without adjusting the pH of the medium. On applying both pseudo first- order and second order kinetics to the adsorption of the dye on SARHC, it was observed that the interactions could be better explained on the basis of first order kinetics. Using SARHC as an adsorbent, the advantage is two fold; it not only acts as an effective and economic tool as compared to other existing commercial carbons for solving the problem of colour pollution but also help in an effective and useful disposal of agriculture waste.

The results point to the effectiveness of the SARHC as an adsorbent for removing dyes like Congo red from solutions of water.

ACKNOWLEDGEMENTS

One of the authors Beena Janveja is greatful to the University Grant Commission, New Delhi, for providing financial assistance under FIP scheme of the UGC to carry out this research work as a part of her Ph.D. thesis.

REFERENCES

1. G. McKay, *Am. Dyest. Rep.*, **68** , 29-36(1979).
2. V.J.P Poots and G.McKay, *Water Res.*, **10** , 1061-1006(1996).
3. T.G. Chuah, A. Jumasiah, I. Azni, S. Katayon, S. Y. Thomas Choong, *Desalination.* **175 ,** 305-316(2005).
4. G.K. Bhattacharya and A. Sharma, *Journal of Environmental Management*, **71** , 217-219(2004).
5. C. O'Neill, F.R. Hawkes, N.D. Lourenco, H.M. Pinbeiro and W. Deice, *J. Chem Technol. Bio-teehnol.*, **74 ,** 1009-1018(1999).
6. K.K.H. Choy, G. McKay and J.F. Porter, *Resour, Conserve, Recy.*, **27 ,** 2469-2479(1999).
7. M.P. Gupta and P.K. Bhattacharrya, *J. Chem. Technol. Biotechnol.*, **m 35B** , 23(1985).
8. S.D. Khattri and M.K. Singh, *Water Air Soil Poil,* **120 ,** 283-294(2000).
9. L. Kun-She, L. Chnoong-Kheng and T. Bee-Foong, *App. Biochem. Biotechnol.*, **87 ,** 233-245(2000).
10. R.M. Liversidge, G.J. Lioyd, D.A.J. Wase and C.F. Forster, *Proc. Biochem.*, **32** , 473-477(1997).
11. G. McKay, M.S. Otterburn and A.G. Sweeney, *Water Air Soil Poll.*, **24** , 147-161(1985).
12. A.K. Mittal and S.K. Gupta, *Water Sci. Techonol.*, **34** ,81-87(1996).
13. F. Perineu, J. molinier and A. Gaset, *J. Chem. Technol. Biotechnol.* **32 ,** 749-758(1982).
14. V.N. Singh, G. Mishra and K.K. Panday, *Ind. J. Technol.*, **22** ,70-71(1984)
15. T. Robinson, G. McMullan, R. Marchant and P. Nigam, *Bioresource Technol.*, **77 ,**247 – 255(2001).
16. C.I. Pearce, J.R. Loyd and J.T. Guthrie, *Dyes Pigments,* **58** , 179-196(2003).
17. S.E. Bailey, T.J. Olin, R.M. Bricka and D.D. Adrian, *Water Res.*, **33** , 57-71(1999).
18. R.R. Bansode, J.N. Losso. W.E. Marshall, R.M. Rao and R.J. Portier, *Bioresource Technol.*, **89** , 115-119(2003).
19. Y. Guo, K. Yu, Z. Wang and H. Xu, *Carbon*, **41** , 1645-1687(2000).
20. I.A. Rahman and J. Ismail, *J. mater. Chem.*, **3 ,** 931-934(1993).
21. I.A Rahman, J. Ismail and H. Osman, *J. Mater. Chem.*, **7,** 1505-1509(1997).
22. S.A. Damel, Rice hull-ash as a piazzolanic material, Masters Thesis, Asian Institute of Technology, 1976
23. H. Olmez, Utilization of agriculture and industrial wastes in production of the cement, Samsun : Ondokuz Mayis University, Publ. NO. 47, 1988.
24. K. G. Mansaraly and A.E. Ghaly, *Energy sources,* **20** , 653-663(1998).
25. D.H. Grist, Rice, 5th ed, Longman, London, 1975.
26. Y. Guo, J. Qi, S. Yang, K. Yu, J.Zhao Z. Wang and H.Xu, Mat. *Chem. Physics*, **74 ,** 320-323(2002).
27. U. Sanigok, Inorganic Industrial Chemistry, Istanbul University Press, Istanbul., 1987.
28. T.H. Usmani, T.W.Ahmad, S.Z. Ahmed and A.H.K. Yousufzai, Pakistan *J.Sci. Indus.*, **36** , 236-239(1993).
29. T.H. Usmani, T.W. Ahmad, S.Z. Ahmed and A.H.K. Ousufzai, Pakistan, *J. Sc Indus.*, **36 ,**240-243(1993).
30. R. Suemitsu, R. Uenishi, I. Akshi, and M Nakano, *J. Appl. Polym. Sci.*, **1** , 75-83(1986).
31. W.E. Marshall, E.T. Champagne and W.J. Evans, *J. Environ. Sci. Health*, **A28,** 1977-1992 (1993).
32. C.K. Lee, K.S. Low and S.J. Mah, Adv. Environ. Res., 2 (1998) 351-259.
33. G. McKay, *water Air Soil Poll.*, **29** , 273-283(1986).
34. G.McKay, G. Ramprasad and P.Mowli, *Water Res.* **21** ,375-377(1987).
35. K.S. Low and C.K. Lee, *Bioresource Technol.*, **61** , 121-125(1997).

36. D. Roy, P.N. Greenlaw and B.S. Shane, *J. Environ. Sci. Health*, **A28,** 37-50 (1993).
37. D.P. Tiwari, D.K. Singh and D.N. Saksena, *J. Env. Eng.*, **121** , 479-481(1995).
38. S.P. Mishra, D. Tiwari and R.S. Dubey, *Appl. Radiat Isot.*, **48** , 877-882(1997).
39. P.K. Malik, *Dyes pigments*, **56** , 239-249(2003).
40. W. Nakbanpote, P. Thiravavetyan and C. Kalambaheti, *Mineral Eng.*, **13** , 391-400(2000).
41. W. Nakbanpote, P. Thiravavetyan and C. Kalambaheti, *Mineral Eng.*, **15,** 549-552(2002).
42. C.R.T. Tarley and M.A.Z. Arruda, *Chemosphere*, **54** , 987-995(2004).
43. K.K. Wong, C.K. Lee, K.S. Low and M.J. Haron, *Chemosphere*, **50** , 23-28.
44. K.K. Wong, C.K. Lee, K.S. Low and M.J. Haron, Process Biochem., 39 (2003) 437-445.
45. A.A.M. Daifulla, B.S. Girgis and H.M.H. Gad, *Mat. Lett.*, **57,** 1723-1731(2003).
46. C.R.T. Tarley, S.L.C. Ferreira and M.A.Z. Arruda, *Microchem. J.*, **77 ,** 163-175(2004).
47. Y. Guo, S. Yang, W. Fu, J. Qi, R. Li, Z. Wang and H. Xu, *Dyes Pigments*, **56** ,219-229(2003).
48. Y. Guo, H. Zhang, N. Tao, Y. Liu, J. Qi, Z. Wang and H. Xu, *Mat. Chem. Physics*, **82** , 107-115(2003).
49. S. Lagergren, *Handlingar* **24** , 1(1898).
50. T. Gosset, J.L. Trancart, D.R. Thevenot, *Water Res.* **20** ,21(1986).
51. D.C. Sharma, C.F. Foster, *Bioresource Technol.* **49 ,**31(1994).
52. Y.S. Ho, G. McKay, *J. Environ. Sci. Health,* **A 345 ,** 1179(1999)
53. C.T. Tien, C.P. Huang, in : J.P. Vernet (Ed.), Trace Meals in the Environment, Elsevier, Amsterdam, 1991, p. 295.
54. C. Namasivayam and R.T., Yamuna, *J.Chem. Tech. Biotechnol.*, **53,** 153-157 (1992).
55. C. Namasivayam, N. Muniasamy, K. Gayatri, M. Rani, K. Ranganathan, *Bioresour. Technol.*, **57,** 37-43(1996)
56. C. Namasivayam and D.S.J.E. Arasi, *Chemosphere*, **34** ,401-417(1997)
57. C. Namasivayam and D. Kavitha, *Dyes Pigm.* **54 ,** 47-50(2002)
58. F.C. Wu, R.L. Tseng, R.S. Juang, *J. Hazard. Mater.* **B73 ,** 63-75**(**2000).

(Received: 18 December 2008 Accepted: 24 December 2008 RJC-307)

> Space travel has given us a new appreciation for the Earth. We realize that the Earth is special. We've seen it from afar. We realize that the Earth is the only natural home for man we know of, and that we had better protect it.
>
> —James Erwin, U.S. astrounaut