

## REFERENCES

- Acemioğlu, B., 2005. Batch kinetic study of sorption of methylene blue by perlite. Chemical Engineering Journal. 106(1): 73-81
- Ahmed, M. and Ram, R., 1992. Removal of basic dye from wastewater using silica as an adsorbent. Environmental Pollution. 77(1): 79-86.
- Aksu, Z., 2005. Application of biosorption for the removal of organic pollutants: a review. Process Biochemistry. 40(3-4): 997-1026.
- Aksu, Z. and Çağatay, Ş. Ş., 2006. Investigation of biosorption of Gemazol Turquoise Blue-G reactive dye by dried *Rhizopus arrhizus* in batch and continuous systems. Separation and Purification Technology. 48(1): 24-35.
- Aksu, Z. and Isoglu, I.A., 2006. Use of agricultural waste sugar beet pulp for the removal of Gemazol turquoise blue-G reactive dye from aqueous solution. Journal of Hazardous Materials. 137(1): 418-430.
- Aksu, Z. and Tezer, S., 2000. Equilibrium and kinetic modeling of biosorption of Remazol Black B by *Rhizopus arrhizus* in a batch system: effect of temperature. Process Biochemistry. 36(5): 431-439.
- Al-Ghouti, M.A., Khraisheh, M.A.M., Allen, S.J. and Ahmad, M.N., 2003. The removal of dyes from textile wastewater: a study of the physical characteristics and adsorption mechanisms of diatomaceous earth. Journal Environmental Management. 69(3): 229-238.
- Allen, W., Prescott, W.B., Derby, R.E., Garland, C.E. and Salzman, M., 1973. Determination of color of water and wastewater by means of ADMI color value. Proceeding of the 27<sup>th</sup> Purdue Industrial Wastewater conference. Part II, Purdue University, Lafayette, Indiana: 661-675.
- Aravindhan, R., Rao, J.R. and Nair, B.U., 2007. Removal of basic yellow dye from aqueous solution by sorption on green alga *Caulerpa scalpelliformis*. Journal of Hazardous Materials. 142(1-2): 68-76.
- Azizian, S., 2004. Kinetic models of sorption: a theoretical analysis. Journal of Colloid and Interface Science. 276(1): 47-52.
- Banat, F., Al-ashah, S. and Al-Makhadmeh, L., 2003. Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters. Process Biochemistry. 39 (2): 193-202.

- Bhattacharyya, K.G. and Sharma A., 2005. Kinetics and thermodynamics of Methylene Blue adsorption on Neem (*Azadirachta indica*) leaf powder'. Dyes and Pigments. 65(1): 51-59.
- Borba, C.E., Guirardello, R., Silva, E.A., Veit, M.T. and Tavares, C.R.G., 2006. Removal of nickel (II) ions from aqueous solution by biosorption in a fixed bed column: Experimental and theoretical breakthrough curves. Biochemical Engineering Journal. 30(2): 184-191.
- Brunauer, S., Deming, L.S., Deming, W.S. and Teller, E. 1940. On a Theory of the van der waals adsorption of gases. Journal of the American Chemical Society. 62(7): 1723-1732.
- Choy, K.K.H., McKay, G., Porter, J.F., 1999. Sorption of acid dyes from effluents using activated carbon. Resources, Conservation and Recycling. 27(1-2): 57-71.
- Chu, H.C. and Chen, K.M., 2002. Reuse of activated sludge biomass: II The rate processes for the adsorption of basic dyes on biomass. Process Biochemistry. 37(10): 1129-1134.
- Crank, J., 1956. The Mathematics of Diffusion. Oxford University Press, London
- Crist, R.H., Oberholser, K., Shank, N. and Nguyeh, M., 1981. Nature of bonding between metallic ions and algal cell walls, Environmental Science and Technology. 15(10): 1212-1217.
- Doğan, M., Alkan, M., Türkyilmaz, A. and Özdemir, Y., 2004. Kinetics and mechanism of removal of methylene blue by adsorption onto perlite. Journal of Hazardous Material. 109(1-3): 141-148.
- Dubinin, M. M., 1966. Modern state of theory of gas vapour adsorption by microporous adsorbents: Pure and Applied Chemistry. 10(1): 309-321.
- Eckenfelder, W.W., Bowers, A.R., Ruth, J.A, 2007. Chemical oxidation for the nineties. Proceeding of the Second International Symposium. Vanderbilt University, Nashville, Tennessee: 161-193.
- Farah, J.Y., Sh.El-Gendy, N. and Farahat, L.A., 2007. Biosorption of Astrazone Blue basic dye from an aqueous solution using dried biomass of Baker's yeast. Journal of Hazardous Materials. 148(1-2): 402-408.
- Faust, S.D., Aly, O.M., 1987. Adsorption process for water treatment. Butterworths, Boston, USA.
- Freundlich, H.M.F., 1906. Über die adsorption in lösungen. Zeitschrift fr

Physikalische Chemie (Leipzig), 57A, 385-470.

- Fu, Y.Z. and Viraraghavan, T., 2000. Removal of a dye from an aqueous solution by the fungus *Aspergillus niger*. Water Quality Research Journal of Canada. 35(1): 95-111.
- Fu, Y.Z. and Viraraghavan, T., 2002. Removal of Congo Red from an aqueous solution by fungus *Aspergillus niger*. Advances in Environmental Research. 7(1): 239-247.
- Garg, V.K., Kumar, R. and Gupta, R., 2004. Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: a case study of *Prosopis cineraria*. Dyes and Pigments. 62 (1): 1-10.
- Gong, R., Ding, Y., Li, M., Yang, C., Liu, H. and Sun, Y., 2005. Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution. Dyes and Pigments. 64(3): 187-192.
- Gong, R., Zhang, X., Liu, H., Sun, Y. and Liu, B., 2007. Uptake of cationic dyes from aqueous solution by biosorption onto granular kohlrabi peel. Bioresource Technology. 98(6): 1319–1323.
- Gregg, S.J. and Sing, K.S.W., 1982. Adsorption, surface area and porosity, 2<sup>nd</sup> ed, 4th printing. Academic Press, London.
- Gupta, V.K., Srivastava, S.K. and Tyagi, R., 2000. Design parameters for the treatment of phenolic wastes by carbon columns (obtained from fertilizer waste material). Water Research. 34(5): 1543–1550.
- Gupta, V.K., Ali, I., Suhas and David, M., 2003. Equilibrium Uptake and Sorption Dynamics for the Removal of a Basic Dye (Basic Red) Using Low Cost Adsorbents. Journal of Colloid and Interface Science. 256(2): 257-264.
- Gupta, V.K., Alok, M. and Vibha, G., 2005. Adsorption and desorption studies of a water soluble dye, Quinoline yellow, using waste materials. Journal of Colloid and Interface Science. 284(1): 89-98.
- Han, R., Wang, Y., Han, P., Shi, J., Yang, J. and Lu, Y., 2006. Removal of methylene blue from aqueous solution by chaff in batch mode. Journal of Hazardous Materials. 137(1): 550-557.
- Ho, Y.S. 2003. Removal of copper ions from aqueous solution by tree fern. Water Research. 37(10): 2323–2330.
- Ho, Y.S., Chiang T.H. and Hsueh Y.M., 2005. Removal of basic dye from aqueous

- solution using tree fern as a biosorbent. Process Biochemistry. 40(1): 119-124.
- Ho, Y.S. and McKay, G., 1998a. Kinetic model for the sorption of dye from aqueous solution by wood. Process Safety and Environmental Protection. 76(B2): 183-191.
- Ho, Y.S. and McKay, G., 1998b. Sorption of dye from aqueous solution by peat, Chemical Engineering Journal. 70(2): 115-124.
- Ho, Y.S. and McKay, G., 1998c. The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat. The Canadian Journal of Chemical Engineering. 76: 822-827.
- Ho, Y.S. and McKay, G., 1999. A kinetic study of dye sorption by biosorbent waste product pith. Resources, Conservation and Recycling. 15(3-4): 171-193.
- Ho, Y.S., Chaing, C.C. and Hsu, Y.C., 2001. Sorption kinetics for dye removal from aqueous solution using activated clay. Separation Science and Technology. 36(11): 2473-2488.
- Hu, T.L., 1992. Sorption of reactive dyes by *Aeromonas* biomass. Water Science and Technology. 26(1-2): 357-366.
- Inbaraj, B.S. and Sulochana, N., 2004. Carbonised jackfruit peel as an adsorbent for the removal of Cd(II) from aqueous solution. Bioresource Technology. 94(1): 49-52.
- Inthorn, D., Singtho, S., Thiravetyan, P. and Khan, E., 2004. Decolorization of basic, direct and reactive dyes by pre-treated narrow-leaved cattail (*Typha angustifolia* Linn.). Bioresource Technology. 94(3): 299-306.
- Khattri, S.D. and Singh, M.K., 1999. Color removal from dye wastewater using sugar cane dust as an adsorbent. Adsorption Science and Technology. 17(1): 269-278.
- Kiselev, A.V. J. 1968. Adsorption properties of hydrophobic surfaces. Journal of Colloid and Interface Science. 28(3): 430-442.
- Kratochvil, D. and Volesky, B., 1998. Biosorption of Cu from ferruginous wastewater by algal biomass. Water Research. 32(9), 2760-2768.
- Kumar, K.V. and Kumaran, A., 2005. Removal of methylene blue by mango seed kernel powder. Biochemical Engineering Journal. 27(1): 83-93.
- Kumar, B.G.P., Miranda, L.R. and Velan, M., 2005a. Adsorption of Bismark Brown dye on activated carbons prepared from rubberwood sawdust (*Hevea*

- brasiliensis*) using different activation methods. Journal of Hazardous Materials. 126(1-3): 63-70.
- Kumar, K.V., Porkodi, K., 2007. Mass transfer, kinetics and equilibrium studies for the biosorption of methylene blue using *Paspalum notatum*. Journal of Hazardous Materials. 146(1-2): 214-226.
- Kumar, K.V., Sivanesan, S. and Ramamurthi, V., 2005. Adsorption of malachite green onto *Pithophora* sp., a fresh water algae: Equilibrium and kinetic modeling. Process Biochemistry. 40(8): 2865-2872.
- Kumar, M.N.V.R., Sridhari, T.R., Bhavani, K.D. and Dutta, P.K., 1998. Trends in color removal from textile mill effluents. Colourage. 40: 25-34.
- Kouba, J.F. and Zhuang, P., 1994. Color removal for textile dyeing wastewater. Fluid/Particle Separation Journal. 7(3): 87-90.
- Lagergren, S., 1898. 'Zur Theorie der sogenannten adsorption gelöster stoffe'. Kungliga Svenska Vetenskapsakademiens Handlingar, Band 24, No. 4.
- Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. Journal of American Chemical Society. 40(9): 1361-1403.
- Lee, C. K., Low, K. S. and Chow, S. W., 1996. Chrome sludge as an adsorbent for colour removal. Environmental Technology. 17 (9), 1023-1028.
- Lin, S.H. and Lin, C.M., 1993. Treatment of textile waste effluent by ozonation and chemical coagulation. Water Research. 27(12): 1743-1748.
- Little, L.W. and Lamb, J.C., 1972. Acute toxicity of 46 selected dyes to the fathead minnow (*Pimephales promelas*). American Dye Manufacturers Institute.
- Liversidge, R.M., Lloyd, G.J., Wase, D.A.J. and Forster, C.F., 1997. Removal of basic blue 41 Dye from aqueous solution by linseed cake. Process Biochemistry. 32(6): 473-477.
- Low, K.S., Lee, C.K. and Tan, K.K., 1995. Biosorption of basic dyes by water hyacinth roots. Bioresource Technology. 52(1): 79-83.
- Magdy, Y.H. and Daifullah, A.A.M., 1998. Adsorption of a basic dye from aqueous solutions onto sugar-industry-mud in two modes of operations. Waste Management. 18(4): 219-226.
- Maurya, N.S., Mittal, A.K., Cornel, P. and Rother, E., 2006. Biosorption of dyes using dead macro fungi: Effect of dye structure, ionic strength and pH. Bioresource Technology. 97(3): 512-521.

- McKay, G., El Geundi, M. and Nassar, M.M., 1987. Equilibrium studies during the removal of dyestuffs from aqueous solutions using bagasse pith. Water Research. 21(12): 1513-1520.
- McKay, G., Porter, J.F. and Prasad, G.R., 1999. The removal of dye colours from aqueous solutions by adsorption on low-cost materials. Water Air and Soil Pollution. 114(3-4): 423-438.
- McKay, G., El-Geundi, M. and Nassar, M.M., 2003. Equilibrium studies during the removal of dyestuffs from aqueous solutions using bagasse pith. Water Research. 21(12): 1513-1520.
- Mishra, G., Tripathy, M., 1993. A critical review of the treatments for decolourization of textile effluent. Colourage. 40: 35-38.
- Mohan, S.V., Ramanaihah, S.V. and Sarma, P.N., 2008. Biosorption of direct azo dye from aqueous phase onto *Spirogyra sp.* I02: Evaluation of kinetics and mechanistic aspects. Biochemical Engineering Journal. 38(1): 61-69.
- Nacéra, Y. and Aicha, B., 2006. Equilibrium and kinetic effluent of methylene blue biosorption by pretreated dead *streptomyces rimosus*: Effect of temperature. Chemical Engineering Journal. 119(2-3): 121-125.
- Namasivayam, C. and Kanchana, N., 1992. Waste banana pith as adsorbent for color removal from wastewaters. Chemosphere. 25(11): 1691-1705.
- Namasivayam, C. and Kavitha, D., 2002. Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. Dyes and Pigments. 54(1): 47-58.
- Namasivayam, C., Muniasamy, N., Gayatri, K., Rani, M. and Ranganathan, K., 1996. Removal of dyes from aqueous solutions by cellulosic waste orange peel. Bioresource Technology. 57(1): 37-43.
- Namasivayam, C., Radhika, R. and Suba, S., 2001. Uptake of dyes by a promising locally available agricultural solid waste: coir pith. Waste Management. 21(4): 381-387.
- Namasivayam, C. and Sumithra S., 2005. Removal of direct red 12B and methylene blue from water by adsorption onto Fe (III)/Cr (III) hydroxide, an industrial solid waste. Journal of Environmental Management. 74(3): 207-215
- Namboodri, C.G., Walsh, W.K., 1996. Ultraviolet light/hydrogen peroxide system for decolorizing spent reactive dye bath waste water. American Dyestuff Reporter.

85(1): 15-25.

- Nassar, M.M., Hamoda, M.F. and Radwan, G.H., 1995. Adsorption equilibria of basic dyestuff onto palm-fruit bunch particles. Water Science and Technology. 32(11): 27-32.
- Nassar, M.M. and Magdy, Y.H., 1997. Removal of different basic dyes from aqueous solutions by adsorption on palm-fruit bunch particles. Chemical Engineering Journal. 66(3): 223-226.
- Nigam, P., Armour, G., Banat. I.M., Singh, D. and Marchant, R., 2000. Physical removal of textile dyes and solid state fermentation of dye adsorbed agricultural residues. Bioresource Technology. 72(3): 219-226.
- Özacar, M. and Şengil, I.A., 2005. Adsorption of metal complex dyes from aqueous solutions by pine sawdust. Bioresource Technology. 96(7): 791-795.
- Padmesh, T.V.N., Vijayaraghavan, K., Sekaran, G. and Velan, M., 2006. Biosorption of Acid Blue 15 using fresh water macroalga *Azolla filiculoides*: Batch and column studies. Dyes and Pigments. 71(2): 77-82.
- Pak, D. and Chang, W., 1999. Decolorizing dye wastewater with low temperature catalytic oxidation. Water Science and Technology. 40(4-5): 115-121.
- Patel, R. and Suresh, S., 2008. Kinetic and equilibrium studies on the biosorption of reactive black 5 dye by *Aspergillus foetidus*. Bioresource Technology. 99(1): 51-58.
- Pavan, F.A., Lima, E.C., Dias, S.L.P. and Mazzocato, A.C., (In Press) Methylene blue biosorption from aqueous solutions by yellow passion fruit waste. Journal of Hazardous Materials, doi:10.1016/j.jhazmat.2007.05.023.
- Peralto-Zamora, P., Kunz, A., Gomez de Morales, S., Pelegrini, R., de Capos Moleiro, P., Reyes, J. and Duran, N., 1999. Degradation of reactive dyes I. A comparative study of ozonation, enzymatic and photochemical processes. Chemosphere. 38(4): 835-852.
- Polman, A. and Brekenridge, C.R., 1996. Biomass-mediated binding and recovery of textile dyes from waste effluents. Textile Chemist and Colorist. 28(4): 31-35.
- Ponnusami, V., Vikram, S. and Srivastava, S.N., (In Press) Guava (*Psidium guajava*) leaf powder: Novel adsorbent for removal of methylene blue from aqueous solutions. Journal of Hazardous Materials. Doi:10.1016/j.jhazmat.2007.06.107
- Punjongharn, P., Meevasana, K. and Pavasant, P., (In Press) Influence of Particle Size

- and Salinity on Adsorption of basic dyes by agricultural waste: dried seagrape (*Caulerpa lentillifera*), Journal of Environmental Sciences. (is scheduled to be published in Vol.20, No.6, 2008)
- Raghavacharya, C., 1997. Colour removal from industrial effluents: a comparative review of available technologies. Chemical Engineering World. 32(1): 53-54.
- Robinson, T., McMullan, G., Maechant, R. and Nigam, P., 2001. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresource Technology. 77(3): 247-255.
- Saniz-Diaz, C. and Griffiths, A., 2000. Activated carbon from solid wastes using a pilot-scale batch flaming pyrolyser. Fuel. 79(15): 1863–1871.
- Sarkar, M., Acharya, P.K. and Bhattacharya, B., 2003. Modeling the adsorption kinetics of some priority organic pollutants in water from diffusion and activation energy parameters. Journal of Colloid and Interface Science. 266(1): 28-32.
- Skoog, D.A. and Leary J.J., 1992. Principles of instrumental analysis, 4<sup>th</sup> ed., Harcourt Publishers, Fort Worth, TX.
- Shawabkeh, A. and Tutunji, M.F., 2003. Experimental study and modeling of basic dye sorption by diatomaceous clay'. Applied Clay Science. 24(1-2): 111-120.
- Slokar, Y.M. and Le Marechal, A.M., 1997. Methods of decolouration of textile wastewaters. Dyes and Pigments. 37(4): 335–356.
- Sungkhum, V., 2003. Biosorption of heavy metals by green macroalga, *Caulerpa lentillifera*. M.Sc. Thesis, Environmental Science, Inter-department of Environmental Science, Graduate School, Chulalongkorn University
- Thomas, H.C., 1944. Heterogeneous ion exchange in a flowing system. Journal of American Chemical Society. 66(10): 1664-1666.
- Tsezos, M. and Bell, J.P., 1989. Comparison of the biosorption and desorption of hazardous organic pollutants by live and dead biomass. Water Research. 23(5): 561-568.
- U.S. EPA, 1996. Best management practice for pollution prevention in the textile industry. EPA/625/R-96/004, Ohio.
- Vadivelan, V. and Kumar, K.V., 2005. Equilibrium, kinetics, mechanism and process design for the sorption of methylene blue onto rice husk. Journal of Colloid and Interface Science. 286(1): 90-100.

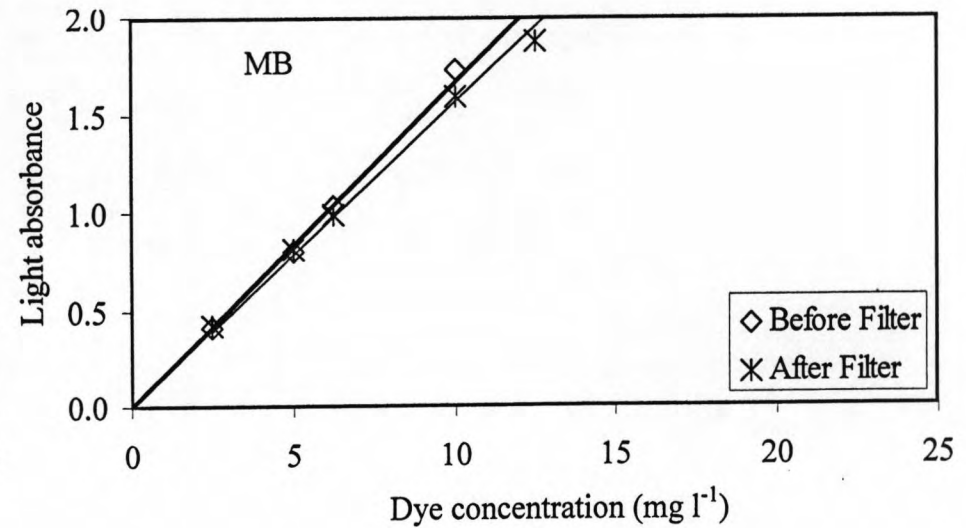
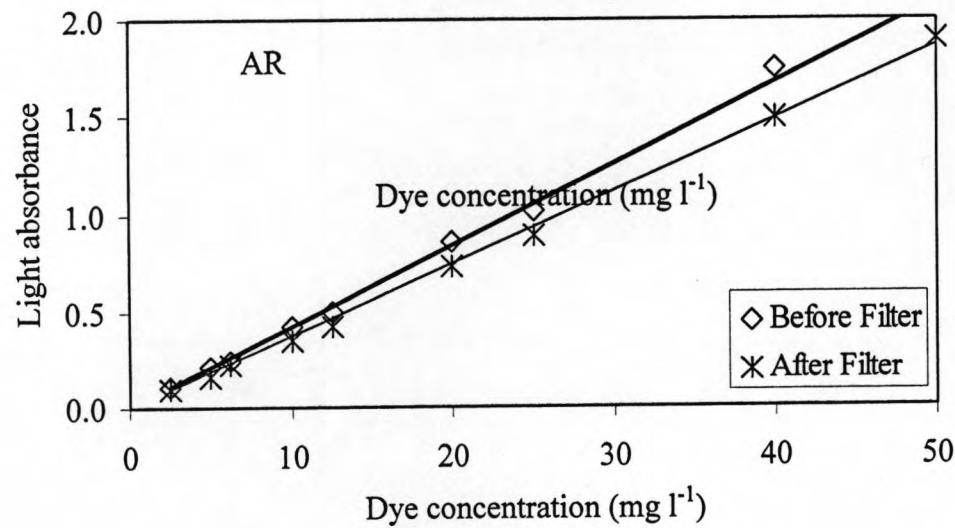
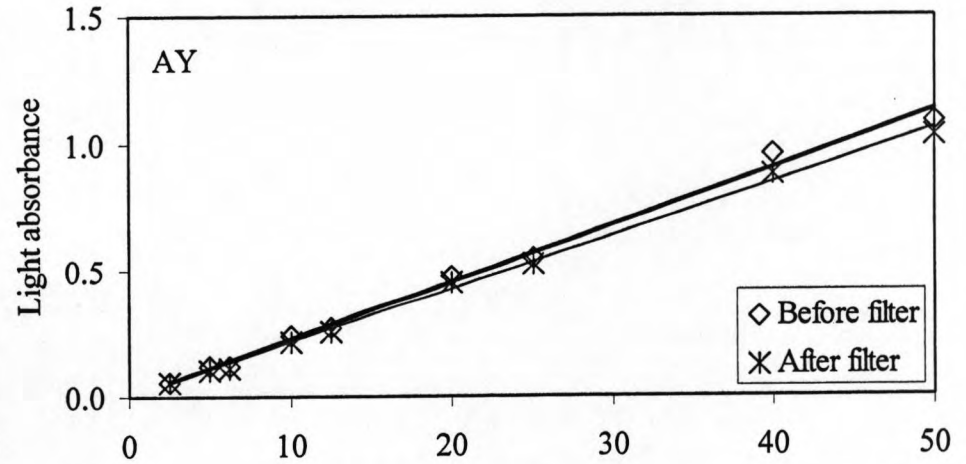
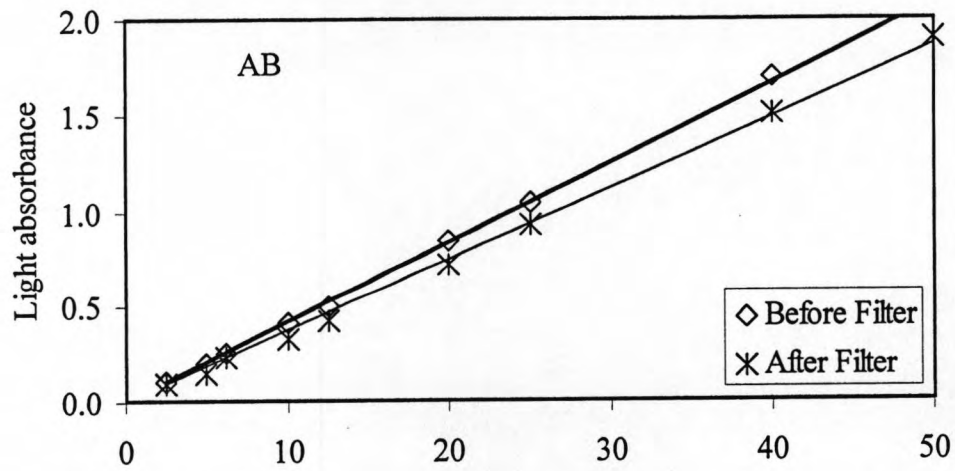


- Volesky, B. 1990. Biosorption of Heavy Metals. CRC Press, Boston.
- Walsh, G.E., Bahner, L.H., and Horning, W.B., 1980. Toxicity of textile mill effluent to freshwater and estuarine algae, crustaceans and fishes. Environmental Pollution Series A. 21(3): 169-179.
- Waranusantigul, P., Pokethitiyook, P., Kruatrachue, M. and Upatham, E.S., 2003. Kinetic of basic dye (methylene blue) biosorption by giant duckweed (*Spirodela polyrrhiza*). Environmental Pollution. 125 (3): 385-392.
- Weber, W.J. and Morris, J.C., 1963. Kinetics of adsorption on carbon from solutions. Journal of the Sanitary Engineering Division, American Society of Civil Engineers. 89(SA2): 31-60.
- Woolard, C.D., Strong, J. and Erasmus, C.R., 2002. Evaluation of the use of modified coal ash as a potential sorbent for organic waste streams, Applied Geochemistry. 17(8), 1159-1164.
- Xu, Y., Lebrun, R.E., Gallo, P.J. and Blond, P., 1999. Treatment of textile dye plant effluent by nanofiltration membrane. Separation Science and Technology. 34(13): 2501-2519.
- Yang, Y., Wyatt, D.T. and Bahorsky, M., 1998. Decolorization of dyes using UV/H<sub>2</sub>O<sub>2</sub> photochemical oxidation. Textile Chemist and Colorist. 30(4): 27-35.
- Yesilada, O., Cing, S. and Asma, D., 2002. Decolourization of the textile dye Astrazon Red FBL by *Funalia trogii* pellets. Bioresource Technology. 81(2): 155-157.
- Zollinger, H., 1987. Colour chemistry-synthesis, properties and application of organic dyes and pigments. VCH Publishers, NewYork.

## **APPENDICES**

## APPENDIX A

Calibration curves of basic dyes: Astrazon® Blue FGRL (AB), Astrazon® Red GTLN (AR), Astrazon® Golden Yellow GL-E (AY), and methylene blue (MB)



## APPENDIX B

Product specification of the chosen commercial activated Carbon

บ.รวมเคมี 1986 จก.

209 - 219 ถนนटनाว แขวงบวรนิเวศน์ เขตพระนคร กทม. 10200

โทร. 02-224-1822-4, 02-224-1803-4 โทรสาร 02-224-6501

<b>Certificate of Analysis</b>	หมายเลขเอกสาร : F-Q-003	R02
	วันที่มีผลบังคับใช้ : 01/03/46	แผ่นที่ 1/1

Activated carbon

DATE : 03/11/2003

PRODUCT NAME : 12 x 40 CGC-16

LOT NUMBER : 4604/104

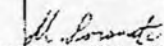
MANUFACTURING DATE : 04/2003

QUANTITY : 125 Kgs.

PACKING : 25 Kgs./BAG

## TECHNICAL CHARACTERISTIC REPORT

PARAMETER	SPECIFICATION	UNIT	RESULT	METHOD
MOISTURE	MAX 5	%	4.9	ASTM D 2867
ASH CONTENT	-	%	2.3	ASTM D 2866
pH VALUE	-		10.2	ASTM D 3838
APPARENT DENSITY	-	gm/cc	0.47	ASTM D 2854
CARBON TETRACHLORIDE ACTIVITY	60-65	%	62.3	ASTM D 3467
IODINE ABSORPTION	-	mg/gm	1151.8	ASTM D 4607
BALL-PAN HARDNESS	-	%	98.8	ASTM D 3802
PARTICLE SIZE DISTRIBUTION	MAX 5	%	+12 = 3.0	ASTM D 2862
	-		12-40 = 95.5	
	MAX 5		-40 = 1.5	



Authorized Name

## APPENDIX C

## Raw data

## C.1 Batch experiments

Experimental conditions: ini.conc 100 mg l<sup>-1</sup>, pH=7, contact time= 1h, shaking speed 130 rpm

Temp (°C)	Weight of alga (g)	Absorbance		
		I	II	III
18	0.1	1.214	1.215	1.231
	0.2	0.853	0.864	0.840
	0.5	0.422	0.421	0.416
	0.7	0.321	0.314	0.312
	0.9	0.202	0.199	0.201
27	0.1	1.253	1.052	1.109
	0.2	0.504	0.495	0.510
	0.5	0.266	0.262	0.305
	0.7	0.198	0.201	0.207
	0.9	0.100	0.142	0.150
40	0.1	0.854	0.842	0.860
	0.2	0.401	0.405	0.402
	0.5	0.195	0.201	0.204
	0.7	0.131	0.135	0.140
	0.9	0.095	0.101	0.102
50	0.1	0.501	0.524	0.588
	0.2	0.321	0.332	0.320
	0.5	0.115	0.124	0.122
	0.7	0.098	0.095	0.108
	0.9	0.079	0.072	0.069
70	0.1	0.497	0.455	0.460
	0.2	0.239	0.241	0.250
	0.5	0.096	0.0850	0.072
	0.7	0.071	0.068	0.070
	0.9	0.048	0.045	0.05

Experimental conditions: initial concentration = 100 mg l<sup>-1</sup>, pH=7, contact time=1h, shaking speed=130 rpm, temperature=27°C

System	Weight of alga (g)	Absorbance	Dilution
CARBON/AB	0.05	1.324	20x
	0.10	1.197	20x
	0.20	1.023	20x
	0.50	0.789	10x
	0.70	0.988	3x
	0.90	0.204	3x
	1.20	0.123	1x
	1.50	0.043	1x
	1.70	0.004	1x
CARBON/AR	0.05	1.347	20x
	0.10	1.103	20x
	0.20	0.402	20x
	0.50	0.217	10x
	0.70	0.547	3x
	0.90	0.465	2x
	1.20	0.876	1x
	1.50	0.977	1x
	1.70	0.023	1x
CARBON/MB	0.05	1.347	20x
	0.10	0.987	20x
	0.20	0.733	10x
	0.50	0.7	3x
	0.70	0.923	2x
	0.90	0.652	2x
	1.20	1.025	2x
	1.50	1.35	1x
	1.70	0.728	1x

Experimental conditions: initial concentration = 100 mg l<sup>-1</sup>, pH=7, contact time=1h, shaking speed=130 rpm, temperature=27°C

System	Weight of alga (g)	Absorbance	Dilution
ALGA/AB	0.05	2.000	5x
	0.10	1.239	5x
	0.20	0.675	5x
	0.50	0.400	2x
	0.70	0.239	2x
	0.90	0.15	2x
	1.20	0.123	1x
	1.50	0.081	1x
	1.70	0.061	1x
ALGA/AR	0.05	0.855	5x
	0.10	0.543	5x
	0.20	0.333	5x
	0.50	0.197	2x
	0.70	0.168	2x
	0.90	0.179	2x
	1.20	0.1	1x
	1.50	0.055	1x
	1.70	0.049	1x
ALGA/MB	0.05	2.108	1x
	0.10	0.633	1x
	0.20	0.359	1x
	0.50	0.256	1x
	0.70	0.217	1x
	0.90	0.182	1x
	1.20	0.099	1x
	1.50	0.022	1x
	1.70	0.014	1x

## C.2 Column experiments

Experimental conditions: initial concentration = 100 mg l<sup>-1</sup>, pH=7, temperature=27°C

Flow rate = 1.2 ml min<sup>-1</sup> cm<sup>-2</sup>, Bed depth=4 cm

Tube	Time (min)	A	Dilution(x)	Tube	Time (min)	A	Dilution(x)
1	7	0.058	1	45	315	0.590	1
2	14	0.049	1	46	322	0.641	1
3	21	0.047	1	47	329	0.688	1
4	28	0.05	1	48	336	0.702	1
5	35	0.062	1	49	343	0.752	1
6	42	0.064	1	50	350	0.803	1
7	49	0.067	1	51	357	0.849	1
8	56	0.065	1	52	364	0.892	1
9	63	0.063	1	53	371	0.963	1
10	70	0.063	1	54	378	1.001	1
11	77	0.064	1	55	385	1.080	1
12	84	0.064	1	56	392	1.178	1
13	91	0.065	1	57	399	1.347	1
14	98	0.068	1	58	406	1.325	1
15	105	0.067	1	59	413	1.489	1
16	112	0.064	1	60	420	1.534	1
17	119	0.062	1	61	427	1.561	1
18	126	0.067	1	62	434	1.605	1
19	133	0.072	1	63	441	1.640	1
20	140	0.075	1	64	448	1.717	1
21	147	0.075	1	65	455	1.756	1
22	154	0.081	1	66	462	0.665	3
23	161	0.084	1	67	469	0.698	3
24	168	0.086	1	68	476	0.700	3
25	175	0.091	1	69	483	0.704	3
26	182	0.093	1	70	490	0.726	3
27	189	0.102	1	71	497	0.732	3
28	196	0.105	1	72	504	0.745	3
29	203	0.109	1	73	511	0.758	3
30	210	0.130	1	74	518	0.762	3
31	217	0.150	1	75	525	0.789	3
32	224	0.168	1	76	532	0.793	3
33	231	0.226	1	77	539	0.803	3
34	238	0.267	1	78	546	0.816	3
35	245	0.294	1	79	553	0.824	3
36	252	0.318	1	80	560	0.834	3
37	259	0.378	1	81	567	0.839	3
38	266	0.389	1	82	574	0.843	3
39	273	0.408	1	83	581	0.852	3
40	280	0.457	1	83	588	0.855	3
41	287	0.489	1	83	595	0.859	3
42	294	0.495	1	83	602	0.863	3
43	301	0.543	1	83	609	0.864	3
44	308	0.567	1				



Flow rate =  $2.4 \text{ ml min}^{-1} \text{ cm}^{-2}$ , Bed depth = 4 cm

Flow rate =  $3.6 \text{ ml min}^{-1} \text{ cm}^{-2}$ , Bed depth = 4 cm

Tube	Time (min)	A	Dilution(x)	Tube	Time (min)	A	Dilution(x)
1	3	0.028	1	1			
2	6	0.037	1	2			
3	9	0.055	1	3			
4	12	0.054	1	4			
5	15	0.054	1	5			
6	18	0.042	1	6			
7	21	0.048	1	7			
8	24	0.043	1	8			
9	27	0.049	1	9			
10	30	0.052	1	10			
11	33	0.05	1	11			
12	36	0.042	1	12			
13	39	0.051	1	13			
14	42	0.057	1	14			
15	45	0.048	1	15			
16	48	0.045	1	16			
17	51	0.047	1	17			
18	54	0.042	1	18			
19	57	0.046	1	19			
20	60	0.048	1	20			
21	63	0.053	1	21			
22	66	0.085	1	22			
23	69	0.094	1	23			
24	72	0.098	1	24			
25	75	0.100	1	25			
26	78	0.125	1	26			
27	87	0.303	1	27			
28	96	0.390	1	28			
29	102	0.512	1	29			
30	114	0.857	1	30			
31	126	0.986	1	31			
32	138	1.125	1	32			
33	147	1.365	1	33			
34	156	1.689	1	34			
35	165	2.121	1	35			
36	174	2.356	1	36			
37	183	2.565	1	37			
38	192	2.689	1	38			
39	201	1.423	2	39			
40	210	1.445	2	40			
41	219	1.468	2	41			
42	228	1.498	2	42			
43	237	1.524	2	43			
44	246	1.547	2	44			

Flow rate =  $1.2 \text{ ml min}^{-1} \text{ cm}^{-2}$ , Bed depth = 6 cm

Flow rate =  $2.4 \text{ ml min}^{-1} \text{ cm}^{-2}$ , Bed depth = 6 cm

Tube	Time (min)	A	Dilution(x)	Tube	Time (min)	A	Dilution(x)
1	5	0.004	1	1	4	0.000	1
2	61	0.005	1	2	36	0.000	1
3	222	0.004	1	3	76	0.000	1
4	334	0.002	1	4	120	0.000	1
5	481	0.005	1	5	168	0.000	1
6	565	0.008	1	6	192	0.012	1
7	614	0.014	3	7	208	0.034	1
8	628	0.024	3	8	216	0.057	1
9	656	0.048	3	9	228	0.104	1
10	670	0.059	3	10	240	0.140	1
11	684	0.067	3	11	252	0.154	1
12	698	0.087	3	12	276	0.247	1
13	712	0.095	3	13	288	0.101	3
14	740	0.125	3	14	300	0.137	3
15	754	0.151	3	15	312	0.208	3
16	768	0.159	3	16	324	0.244	3
17	810	0.207	3	17	336	0.275	3
18	838	0.246	3	18	348	0.314	3
19	866	0.289	3	19	360	0.401	3
20	894	0.304	3	20	372	0.412	3
21	908	0.345	3	21	384	0.497	3
22	922	0.367	3	22	396	0.524	3
23	936	0.395	3	23	408	0.541	3
24	957	0.409	3	24	432	0.621	3
25	978	0.428	3	25	448	0.684	3
26	999	0.457	3	26	468	0.732	3
27	1041	0.497	3	27	484	0.754	3
28	1097	0.547	3	28	496	0.785	3
29	1111	0.567	3	29	504	0.802	3
30	1181	0.652	3	30	520	0.825	3
31	1223	0.697	3	31	488	0.000	3
32	1272	0.726	3	32	492	0.000	3
33	1314	0.769	3	33	536	0.864	3
34	1377	0.802	3	34	548	0.887	3
35	1419	0.830	3	35	560	0.892	3
36	1461	0.857	3	36	576	0.905	3
37	1510	0.895	3	37	592	0.923	3
38	1545	0.912	3	38	604	0.937	3
39	1587	0.926	3	39	616	0.946	3
40	1650	0.958	3	40	632	0.952	3
41	1713	0.969	3	41	648	0.967	3
42	1762	0.992	3	42	664	0.969	3
43	1825	1.005	3	43	692	0.977	3
44	1881	1.014	3				
45	1909	1.017	3				

Flow rate =  $3.6 \text{ ml min}^{-1} \text{ cm}^{-2}$ , Bed depth = 6 cm

Flow rate =  $1.2 \text{ ml min}^{-1} \text{ cm}^{-2}$ , Bed depth = 8 cm

Tube	Time (min)	A	Dilution(x)	Tube	Time (min)	A	Dilution(x)
1	2	0.000	1	1	1491	0.002	1
2	22	0.002	1	2	1589	0.007	1
3	34	0.003	1	3	1673	0.005	1
4	44	0.007	1	4	1750	0.059	1
5	54	0.005	1	5	1764	0.089	1
6	66	0.012	3	6	1778	0.104	1
7	74	0.042	3	7	1806	0.116	1
8	78	0.045	3	8	1827	0.132	1
9	82	0.046	3	9	1848	0.138	1
10	90	0.072	3	10	1869	0.145	1
11	96	0.092	3	11	1897	0.168	1
12	112	0.124	3	12	1925	0.178	1
13	128	0.197	3	13	1953	0.198	1
14	140	0.237	3	14	1974	0.214	1
15	152	0.294	3	15	2009	0.268	1
16	160	0.375	3	16	2030	0.154	3
17	174.5	0.435	3	17	2044	0.152	3
18	189.5	0.507	3	18	2058	0.157	3
19	204.5	0.604	3	19	2079	0.167	3
20	219.5	0.734	3	20	2100	0.178	3
21	229.5	0.760	3	21	2114	0.194	3
22	234.5	0.841	3	22	2135	0.204	3
23	242	0.867	3	23	2156	0.218	3
24	257	0.904	3	24	2205	0.238	3
25	264.5	0.927	3	25	2240	0.258	3
26	269.5	0.941	3	26	2289	0.267	3
27	282	0.967	3	27	2324	0.289	3
28	294.5	0.982	3	28	2373	0.314	3
29	307	1.005	3	29	2408	0.327	3
30	317	1.009	3	30	2471	0.351	3
31	327	1.018	3	31	2513	0.397	3
32	337	1.027	3	32	2555	0.400	3
33	349.5	1.029		33	2611	0.426	3
				34	2674	0.480	3
				35	2765	0.519	3
				36	2842	0.561	3
				37	2898	0.592	3
				38	3038	0.637	3
				39	3164	0.704	3
				40	3241	0.742	3
				41	3325	0.780	3
				42	3409	0.824	3
				43	3465	0.834	3
				44	3542	0.849	3
				45	3605	0.857	3

*Flow rate = 1.2 ml min<sup>-1</sup> cm<sup>-2</sup>, Bed depth= 8 cm  
(Cont.)*

Tube	Time (min)	A	Dilution(x)
46	3640	0.872	3
47	3745	0.885	3
48	3815	0.891	3
49	3892	0.902	3
50	3969	0.915	3
51	4004	0.927	3

*Flow rate = 2.4 ml min<sup>-1</sup> cm<sup>-2</sup>, Bed depth=8 cm*

Tube	Time (min)	A	Dilution(x)
1	144	0.001	1
2	232	0.002	1
3	340	0.007	1
4	424	0.018	3
5	520	0.061	3
6	552	0.062	3
7	588	0.062	3
8	616	0.062	3
9	648	0.067	3
10	660	0.074	3
11	672	0.085	3
12	688	0.097	3
13	712	0.124	3
14	744	0.155	3
15	776	0.186	3
16	816	0.221	3
17	856	0.271	3
18	900	0.312	3
19	916	0.358	3
20	944	0.391	3
21	968	0.421	3
22	988	0.435	3
23	1012	0.489	3
24	1064	0.538	3
25	1080	0.587	3
26	1100	0.621	3
27	1120	0.645	3
28	1148	0.731	3
29	1176	0.755	3
30	1224	0.814	3
31	1256	0.867	3
32	1292	0.921	3
33	1316	0.958	3
34	1356	0.994	3
35	1400	1.032	3
36	1448	1.051	3
37	1484	1.055	3

*Flow rate = 3.6 ml min<sup>-1</sup> cm<sup>-2</sup>, Bed depth= 8 cm*

Tube	Time (min)	A	Dilution(x)
1	8	0.002	1
2	58	0.006	1
3	104	0.004	1
4	154	0.016	1
5	304.5	0.1	1
6	314.5	0.125	1
7	324.5	0.175	1
8	334.5	0.25	1
9	359.5	0.4	1
10	399.5	0.245	3
11	429.5	0.314	3
12	454.5	0.367	3
13	477	0.417	3
14	502	0.468	3
15	529.5	0.534	3
16	582	0.679	3
17	622	0.802	3
18	654.5	0.904	3
19	674.5	0.981	3
20	692	1.024	3
21	707	1.039	3
22	727	1.065	3
23	749.5	1.071	3
24	779.5	1.075	3
25	802	1.08	3
26	832	1.082	3
27	874.5	1.083	3
28	907	1.084	3
29	932	1.085	3
30	974.5	1.084	3
31	1002	1.085	3
32	1024.5	1.088	3
33	1097	1.085	3
34	1124.5	1.088	3

## APPENDIX D

### Paper Publications

- D1. **Khanidtha Marungrueng** and Prasert Pavasant, 2006. Removal of basic dye (Astrazon blue FGRL) using macroalga, *Caulerpa lentillifera*. Journal of Environmental Management. 78(3): 268-274.
- D2. **Khanidtha Marungrueng** and Prasert Pavasant, 2007. High performance biosorbent (*Caulerpa lentillifera*) for basic dye removal. Bioresource Technology. 98(8): 1567-1572.
- D3. Pimol Punjonghan, **Khanidtha Meevasana**, Prasert Pavasant, Influence of Particle Size and Salinity on Adsorption of basic dyes by agricultural waste: dried seagrape (*Caulerpa lentillifera*), Journal of Environmental Sciences. *Accepted for publication* (is scheduled to be published in Vol.20, No.6, 2008)

### Conferences

- D3. **Khanidtha Marungrueng** and Prasert Pavasant. Characteristics of fixed bed column for the removal of basic dye with macro alga, *Caulepa lentillifera*. The Regional Symposium on Chemical Engineering (RSCE2004), Bangkok, Thailand, December 1-3, 2004. (Oral presentation)
- D4. **Khanidtha Marungrueng** and Prasert Pavasant. Removal of cationic dyes from synthetic wastewater using *Caulerpa lentillifera*: A comparative study with commercial activated carbon. RGJ Congress VI, Pattaya, Thailand, March 28-30, 2005. (Poster Presentation)
- D5. Pimol Punjongharn, **Khanidtha Marungrueng** and Prasert Pavasant. Effect of sorbent size on the sorption of basic dyes by using *Caulepa lentillifera*. The 2nd Joint International Conference on "Sustainable Energy and Environment (SEE2006)", Bangkok, Thailand, November 21-23, 2006. (Oral presentation)
- D6. **Khanidtha Marungrueng** and Prasert Pavasant. Fixed-bed biosorption column for the removal of basic dye with a promising biosorbent: *Caulepa lentillifera*. The Regional Symposium on Chemical Engineering (RSCE2006), Nanyang University, Singapore, December 2-5, 2006. (Oral presentation)



## Removal of basic dye (Astrazon Blue FGRL) using macroalga *Caulerpa lentillifera*

Khanidtha Marungrueng<sup>a</sup>, Prasert Pavasant<sup>b,\*</sup>

<sup>a</sup>National Research Center for Environmental and Hazardous Waste Management, Chulalongkorn University, 10330 Bangkok, Thailand

<sup>b</sup>Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, 10330 Bangkok, Thailand

Received 1 July 2004; revised 15 March 2005; accepted 12 April 2005

Available online 19 August 2005

### Abstract

The macroalga *Caulerpa lentillifera* was found to have adsorption capacity for a basic dye, Astrazon Blue FGRL. For the whole range of concentrations employed in this work (20–1280 mg l<sup>-1</sup>), the adsorption reached equilibrium within the first hour. The kinetic data corresponded well with the pseudo second-order kinetic model where the rate constants decreased as initial dye concentrations increased. At low dye concentrations (20–80 mg l<sup>-1</sup>), an increase in the adsorbent dosage resulted in a higher removal percentage of the dye, but a lower amount of dye adsorbed per unit mass (*q*). The adsorption isotherm followed both the Langmuir and Freundlich models within the temperature range employed in this work (18–70 °C). The highest maximum adsorption capacity (*q<sub>m</sub>*) was obtained at 50 °C. The enthalpy of adsorption was estimated at 14.87 kJ mol<sup>-1</sup> suggesting a chemical adsorption mechanism.

© 2005 Elsevier Ltd. All rights reserved.

**Keywords:** Textile dye; Adsorption; Decolorization; Green algae; Isotherms; Kinetics; Enthalpy of adsorption

### 1. Introduction

For decades, dyes and pigments have been used for coloring in the textile industry. Several types of textile dyes are available for usage with various types of textile materials. Among these many types, 'cationic dyes', commonly known as basic dyes, are widely used in acrylic, nylon, silk, and wool dyeing. In textile dyeing processes, a large volume of dye-contaminated effluent is discharged, and it was estimated that 10–15% of the dye is lost in the dye effluent (Zollinger, 1987). US EPA (1996) reported that 1,000 mg l<sup>-1</sup> of dye was used in a typical dyebath and 100 mg l<sup>-1</sup> of dye was left in the spent dyebath. The presence of dyes in the effluent at a very low concentration could be highly visible and undesirable (Nigam et al., 2000). The colored wastewater damages the aesthetic nature of water and reduces the light penetration through the water's surface, and also the photosynthetic activity of aquatic organisms.

Textile dyes are relatively resistant to microbial degradation due to their complicated structures (Yesilada et al., 2002). In particular, due to the presence of metals in their structure, basic dyes are considered one of the most toxic substances (US EPA, 1996). Consequently, the removal of dyes from effluents is required. This is usually achieved through physio-chemical means (Robinson et al., 2001). The various treatment methods are oxidation using, for example, Fenton reagent (Pak and Chang, 1999) and ozone (Lin and Lin, 1993), and adsorption using synthetic or natural adsorbents. Adsorption has been found to be superior to other techniques for wastewater treatment in terms of cost, simplicity of design, ease of operation and insensitivity to toxic substances (Garg et al., 2004). The use of natural materials for dye removal is advantageous as they are often available in large quantities. Examples of these materials are bagasse pith for the adsorption of basic blue 69, basic red 22, acid red 114, and acid blue 25 (McKay et al., 1987); banana pith for the adsorption of basic violet from wastewater (Namasivayam and Kanchana, 1992); palm-fruit bunch for the adsorption of basic yellow, basic red and basic blue (Nassar and Magdy, 1997); wheat straw, corncobs and barley husks for the adsorption of Cibacron Yellow C-2R, Cibacron Red C-2G, Cibacron Blue C-R,

\* Corresponding author. Tel.: +662 218 6870; fax: +662 218 6877.  
E-mail address: prasert.p@chula.ac.th (P. Pavasant).

Remazol Black B, and Remazol Red RB (Robinson et al., 2002); duckweed for the adsorption of methylene blue (Waranusantigul et al., 2003); and date pits for the adsorption of methylene blue (Banat et al., 2003).

Algae is an alternative biosorbent of growing interest. In many cases, algal cell walls consisting of proteins and carbohydrates (Crist et al., 1981) provide functional groups that could form bonds with cations such as metals and basic dyes. The macroalga *Caulerpa lentillifera* grows rapidly in rainfed agricultural areas. This particular algal species is often cultivated in a polishing pond of a closed-loop shrimp farm system, as it acts as a natural nitrogen controlling medium. Although some part of fresh *C. lentillifera* can be employed as a nutritional supplement, the rest of the alga can not, and it is often required that farmers remove and dispose of this over-grown alga as an unwanted material. Turning this alga into an adsorbent for basic dyes is therefore presented as a low-cost alternative for the management of this unwanted agricultural material. The purpose of this work was therefore to investigate the adsorption behavior of a basic dye onto *C. lentillifera*. Astrazon Blue FGRL was selected as the modeled basic dye for this work as it is one of the dyes most commonly used in nylon and acrylic textiles. The nature of adsorption, the effects of the adsorbent dosage, the adsorption isotherm, and the enthalpy of adsorption were examined.

## 2. Materials and Methods

### 2.1. Preparation of dried algae

*Caulerpa lentillifera* was collected from Banchong Farm, Chachoengsao province, Thailand. After being washed with deionized water, the alga was dried at 80 °C for 12 h and stored in a desiccator. The functional groups of *C. lentillifera* were interpreted using the Fourier Transform InfraRed (FT-IR) technique (Perkin Elmer, 1760X) and the results are shown in Table 1.

Table 1  
Functional groups in dried *C. lentillifera*

Functional group	Standard Wavenumber (Skoog and Leary, 1992) (cm <sup>-1</sup> )	Wavenumber from the results (cm <sup>-1</sup> )	Relative quantity*
Hydroxyl; O-H	3250–3700	3200–3600	1
Carboxyl; COOH	2400–3300	3200–3600	1
Amine; NH <sub>2</sub>	3300–3500	3200–3600	1
C-O	1050–1300	1000–1200	2
Sulfonyl; S=O	1040–1200	1000–1200	2
Carbonyl; C=O	1670–1780	1600–1750	3
S-O	550–650	500	4
Alkyl; C-H	Carboxylic acid: 2500–3100 Alcohol: 3400–3640	2900–3000	5

\* The quantity in the order from large to small (1 is the most abundant and 5 is the least)

### 2.2. Basic dye Astrazon Blue FGRL

Astrazon Blue FGRL, a cationic dye, was supplied by Dystar Thai Co., Ltd. This commercial dye consists of two main components, which are C.I. basic blue 159 and C.I. basic blue 3. The ratio of the two components is approximately 5:1 by weight, respectively. The structures of these two dye components are shown in Fig. 1. The net charge of both C.I. basic blue 159 and C.I. basic blue 3 is equal to +1. Although Astrazon Blue FGRL is a mixture of two basic components, the following discussion will treat this as a single dye species.

The measurements of the dye concentrations were performed through light absorbance using a Spectronic® UV/VIS Helios Alpha spectrophotometer (operated with Vision32 software -v1.25). The calibration curve was plotted from the dye solutions prepared in the concentration range of 1 to 100 mg l<sup>-1</sup>.

### 2.3. Batch adsorption experiments

The flask containing 0.5 g of alga and 30 ml of dye solution was placed in a shaker operating at 130 rpm. In the adsorption kinetic experiments, samples were taken to measure the dye concentration at predetermined time intervals. The effects of adsorbent dosage were studied by using different weights of alga adsorbent (range from 0.05–1.7 g). The adsorption isotherm was studied at 18, 27, 40, 50 and 70 °C. The shaker water bath (GFL model 1086) was used to maintain the temperature during the adsorption. The flasks were capped in order to prevent evaporation at high temperatures. In all cases, after contacting, the alga was removed from the solution by filtering it through a membrane filter (0.25 µm). Our preliminary work illustrated that the highest light absorbance of Astrazon Blue FGRL occurred at 576 nm; and therefore, the absorbance of the dye solutions was measured at this wavelength throughout this study. The dye removal percentage can be calculated as follows:

$$\text{Removal percentage} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

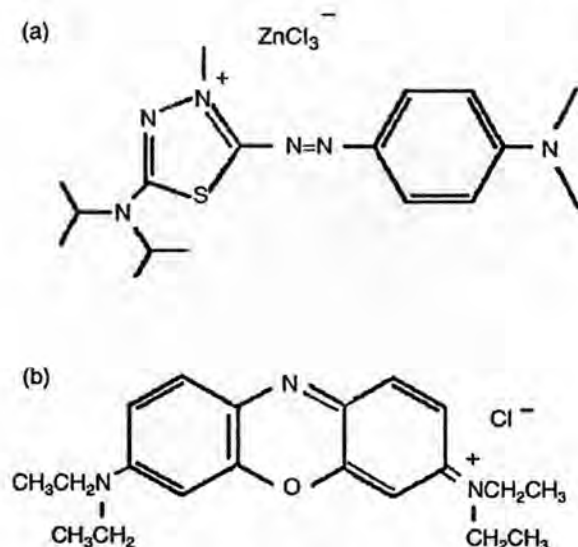


Fig. 1. Chemical structures of (a) C.I. basic blue 159 and (b) C.I. basic blue 3.

where  $C_i$  and  $C_e$  are the initial and equilibrium dye concentrations, respectively. The dye uptake capacity,  $q$ , can also be calculated from the difference between the initial and equilibrium concentrations as shown in the following equation:

$$q = \frac{(C_i - C_e)V}{M} \quad (2)$$

where  $q$  is the adsorbed dye quantity per gram of biomass at any time ( $\text{mg g}^{-1}$ ),  $M$  the adsorbent dosage (g), and  $V$  the solution volume (l).

### 3. Results and Discussion

#### 3.1. Adsorption kinetics

The adsorption kinetics of Astrazon Blue FGRL by *C. lentillifera* at various initial dye concentrations (20, 40, 80, 160, 320, 640, and 1280  $\text{mg l}^{-1}$ ) are shown in Fig. 2. It was

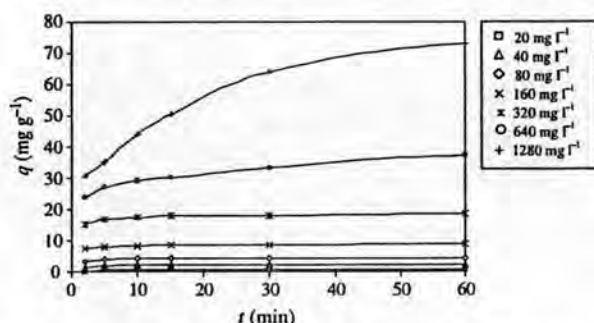


Fig. 2. Kinetics of Astrazon Blue FGRL uptake by *C. lentillifera* (adsorbent dose = 0.5 g, temperature = 27 °C).

observed that the adsorption capacity increased with time, and at a certain time period, reached a constant value indicating that no dye was further removed from the solution. At this point, the amount of dye being adsorbed onto the alga was in a state of dynamic equilibrium with the amount of dye desorbed from the alga. The time it took to reach an equilibrium varied with the initial concentration, i.e., the solution with a higher initial concentration required a slightly longer time than the solution with a lower initial concentration. However, for the range of dye concentrations employed in this work, equilibrium was reached within the first hour of adsorption.

The adsorption capacity at equilibrium was found to be linearly proportional to the initial concentration. This characteristic was also found even with the solution with an extremely high dye concentration. To illustrate this point, the adsorption at a high dye concentration is shown in Fig. 2. The highest concentration of the dye in this experiment was 1,280  $\text{mg l}^{-1}$ , and at this point, the adsorption capacity of the alga was still two times higher than that with the dye concentration of 640  $\text{mg l}^{-1}$ . This indicated that the alga still could accommodate more dye adsorption. However, a higher dye concentration than 1,280  $\text{mg l}^{-1}$  could not be prepared and dealt with easily due to its extremely high viscosity and difficulty in handling. Nevertheless, a dye concentration above 1,280  $\text{mg l}^{-1}$  is far beyond the level found in industrial effluent, which is only approximately 100  $\text{mg l}^{-1}$  (U.S. EPA, 1996). Hence, the adsorption characteristics of a dye solution above 1,280  $\text{mg l}^{-1}$  were not investigated in this work.

In order to characterize the kinetic behavior of a reaction, it is desirable to determine how the rate of reaction varies as the reaction progresses. Lagergren's first order kinetic equation has been most widely used to describe the solute adsorption on various adsorbents (Ho, 2003). The first-order Lagergren expression based on the solid capacity is (Lagergren, 1898)

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

where  $q_e$  and  $q$  are the amount of adsorbed dye on the biosorbent at the equilibrium and at time  $t$ , respectively ( $\text{mg g}^{-1}$ ), and  $k_1$  is the rate constant of first-order biosorption ( $\text{min}^{-1}$ ).

Another widely used kinetic expression is the pseudo second-order rate expression derived by Ho and McKay (Ho and McKay, 2003) where sorption capacity was assumed to be proportional to the number of active sites occupied on the sorbent. The pseudo second-order kinetic rate law can be expressed as:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where  $k_2$  is the pseudo second-order rate constant with a unit of  $\text{g mg}^{-1} \text{min}^{-1}$ .



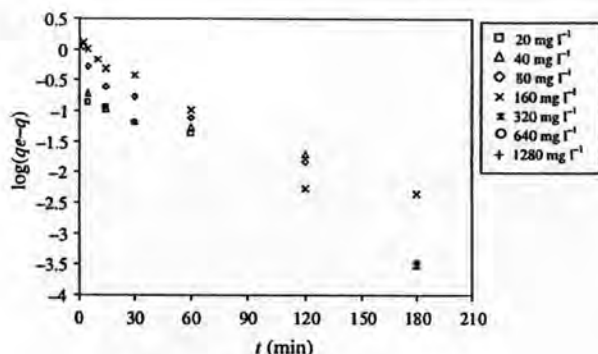


Fig. 3. First-order sorption kinetics of Astrazon Blue FGRL by *C. lentillifera* at various initial dye concentrations (adsorbent dose = 0.5 g, temperature = 27 °C).

The first-order and the pseudo second-order kinetic models were applied to the experimental data. The plots of these two kinetic models at all initial concentrations are illustrated in Figs. 3 and 4, respectively. For the data to follow the first-order kinetics in Eq. (3), the linear plot between  $\log(q_e - q)$  and  $t$  should be observed. However, the results illustrate that this linear dependency could not be obtained indicating that the first-order Lagergren rate kinetics are not appropriate for the adsorption of basic dye on the alga. For the pseudo second-order kinetics, the parameters,  $q_e$  and  $k_2$ , could be determined from the intercept and the slope of the plots in Fig. 4 and these are summarized in Table 2. Extremely good agreement between the results and the model was obtained as illustrated by the very high  $R^2$  for the whole range of initial dye concentrations. Hence, it was concluded at this point that the adsorption here could be better represented by the pseudo second-order rate kinetics. The results also indicated that an increase in the initial dye concentration increased the equilibrium sorption capacity,  $q_e$ , whilst decreasing the rate constant,  $k_2$ .

This finding was similar to other studies on the biosorption of several other dyes. For instance, pseudo second-order kinetics were also observed in the biosorption

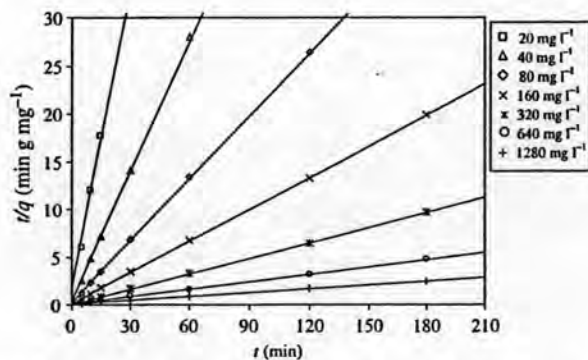


Fig. 4. Pseudo second-order sorption kinetics of Astrazon Blue FGRL by *C. lentillifera* at various initial dye concentrations (adsorbent dose = 0.5 g, temperature = 27 °C).

Table 2

Pseudo second-order rate constants at different initial dye concentrations

$C_i$ (mg l <sup>-1</sup> )	$q_{e,cap}$ (mg g <sup>-1</sup> )	Pseudo second-order rate constants		
		$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$q_{e,cal}$ (mg g <sup>-1</sup> )	$R^2$
20	0.980	$5.56 \times 10^{-1}$	0.981	0.9999
40	2.19	$5.11 \times 10^{-1}$	2.20	1.0000
80	4.56	$4.91 \times 10^{-1}$	4.57	1.0000
160	9.05	$1.18 \times 10^{-1}$	9.10	1.0000
320	18.6	$8.82 \times 10^{-2}$	18.6	1.0000
640	37.8	$8.03 \times 10^{-3}$	38.6	0.9997
1280	73.0	$2.23 \times 10^{-3}$	75.8	0.9993

of Remazol Black B on biomass (Aksu and Tezer, 2000), the adsorption of Congo Red on activated carbon (Namasiyayam and Kavitha, 2002), and methylene blue on perlite (Doğan et al., 2004).

### 3.2. Effects of the adsorbent dosage

In order to examine the effect of the adsorbent dosage on the removal efficiency of Astrazon Blue FGRL, adsorption experiments were set up with various amounts of dried alga (0.05–1.7 g) and dye concentrations (20, 40 and 80 mg l<sup>-1</sup>). The uptake of the dye,  $q$ , and the removal percentage versus the adsorbent dosage,  $M$ , is shown in Fig. 5. Although increasing the adsorbent quantity provided more adsorption sites for the dye, the dye removal percentage did not linearly depend on the adsorbent dosage. For the range of dye concentration examined here, 0.8 g (for 30 ml of dye solution) of dried alga was observed to be the upper limit for the removal of such dye. Increasing the quantity of dried alga above 0.8 g could only marginally raise the dye removal percentage. At this point, however, the dye removal efficiency was more than 95% which was already quite satisfactory. On the other hand, the adsorbed dye quantity per gram of biomass,  $q$ , decreased with an increase in the adsorbent dosage. This was because, with an increase in adsorbent dosage, the residual concentration of the dye in solution decreased. Due to equilibrium limitations, the uptake capacity of dye at low concentrations often was lower than at high concentrations.

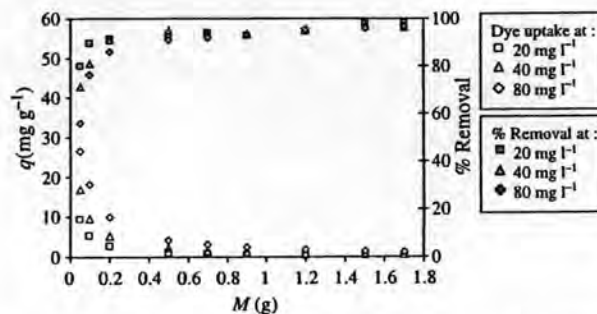


Fig. 5. Effect of adsorbent dosage on the uptake of Astrazon Blue FGRL.

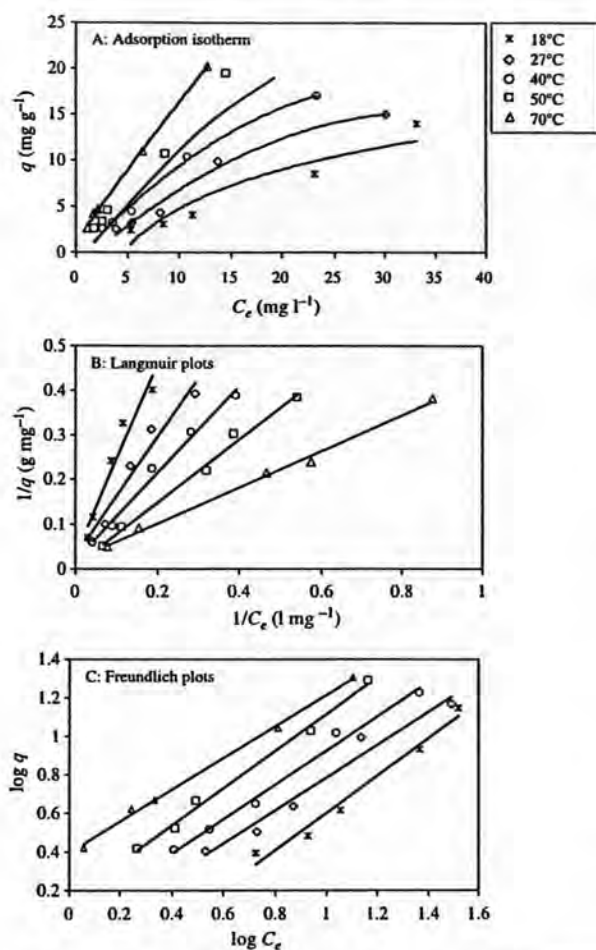


Fig. 6. Langmuir, and Freundlich isotherm plots for adsorption of basic dye, Astrazon Blue FGRL, by *C. lentillifera*.

The differences in adsorption characteristics at different initial dye concentrations were not obvious as illustrated in Fig. 5. At a low adsorbent dosage (algal mass less than 0.8 g), the removal efficiency was slightly higher for the dye solution with a low initial dye concentration. However, at a high adsorbent dosage, the difference in the removal efficiency or adsorption capacity of solutions with various initial dye concentrations could not be clearly distinguished. Equilibrium played a significant role in determining the quantity of dye being adsorbed onto the algal mass and this controlled the removal efficiency of the adsorption process.

Table 3

Constants of Langmuir and Freundlich isotherms for adsorption of Astrazon Blue FGRL by *C. lentillifera*

Temperature (°C)	Langmuir constants			Freundlich constants		
	$q_m$ (mg g <sup>-1</sup> )	$b$ (l mg <sup>-1</sup> )	$R^2$	$K_f$	$n$	$R^2$
18	30.67	0.015	0.9429	0.43	1.04	0.9766
27	37.17	0.020	0.9574	0.77	1.10	0.9734
40	48.65	0.021	0.9881	0.94	1.11	0.9895
50	49.26	0.031	0.9903	1.35	1.10	0.9942
70	46.73	0.053	0.9954	2.39	1.20	0.9954

Equilibrium can be expressed in terms of isotherms as discussed in the next section.

### 3.3. Adsorption isotherms

The adsorption isotherms for Astrazon Blue FGRL and *C. lentillifera*, which represent the equilibrium concentrations in the solid and liquid phases, are illustrated in Fig. 6. Fig. 6 A shows raw data from the experiment at 5 levels of temperature whilst Fig. 6 B and C illustrate the plots according to Langmuir's and Freundlich's isotherm criteria, respectively.

Langmuir's isotherm can be expressed in a mathematical form (Langmuir, 1916; Langmuir, 1918) as shown in Eq. (5). Hence, if the adsorption data follow Langmuir's isotherm, the plot between  $1/q$  and  $1/C_e$  must give a straight line. Langmuir's isotherm is of the form

$$\frac{1}{q} = \frac{1}{q_m} + \left(\frac{1}{bq_m}\right)\left(\frac{1}{C_e}\right) \quad (5)$$

Fig. 6B illustrates that a straight line could be well observed between  $1/q$  and  $1/C_e$  indicating that the experimental data followed Langmuir's isotherm. The maximum adsorption capacity ( $q_m$ ) and the Langmuir constant ( $b$ ) were calculated from this plot and the results are summarized in Table 3.

The Langmuir parameters, i.e.,  $q_m$  and  $b$ , increased with temperature. High temperatures increased the kinetic energy of the dye and, hence, enhanced the mobility of the dye ions. This led to a higher chance of the dye being adsorbed onto the adsorbent and an increase in its adsorption capacity. This agreed well with the findings of Lee et al. (1996). However, an excessively high temperature (70 °C) might not be appropriate for the adsorption of Astrazon Blue FGRL as it could destroy or change the integrity of the alga and reduce the active adsorption sites. In this case,  $q_m$  was dropped from 49.26 mg g<sup>-1</sup> at 50 °C to 46.73 mg g<sup>-1</sup> at 70 °C.

The Freundlich isotherm was constructed based on a different assumption (Freundlich, 1906) from Langmuir's. While Langmuir's adsorption assumed a monolayer adsorption, Freundlich did not and this allowed unlimited adsorption characteristics which could be advantageous for describing the adsorption of a low strength solution. The linearized Freundlich isotherm equation can be written as follows:

$$\log q = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (6)$$

where  $n$  and  $K_f$  are Freundlich constants (Weber, 1972). The linearity of the plot displayed in Fig. 6C suggested the applicability of the Freundlich model. The Freundlich constants, i.e.,  $1/n$  and  $K_f$ , were calculated from the slope and interception of the Freundlich plots, respectively, and the results are also summarized in Table 3. It should be noted that the exponential constants,  $1/n$ , were almost unity, which meant that the dye was favorably adsorbed onto the dried algae.

As both the Langmuir and Freundlich models could explain the adsorption, the adsorption in the range of concentration employed in this work should still be in the monolayer region. Increasing the dye concentration could lead to a clearer difference between the usage of these two models, however, higher dye concentrations than  $100 \text{ mg l}^{-1}$  are highly unlikely to occur in conventional textile wastewater.

### 3.4. Enthalpy of adsorption

The apparent heat or net enthalpy of adsorption,  $\Delta H$ , is related to the Langmuir constant,  $b$ , as present in Eq. (7) (Faust and Aly, 1987):

$$\ln b = \ln b' - \frac{\Delta H}{RT} \quad (7)$$

where  $b'$  is a constant,  $R$  the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ), and  $T$  the temperature in Kelvin. The slope of the plot of  $\ln b$  versus  $1/T$  in Fig. 7 represents  $-\Delta H/R$  and, therefore,  $\Delta H$  could be calculated. Only four sets of experimental data, 18, 27, 40, and  $50^\circ\text{C}$ , were used in this section. The data at  $70^\circ\text{C}$  were not used because such high temperature could reduce the active adsorption sites on the alga surface. For this experiment,  $\Delta H$  took the value of  $14.87 \text{ kJ mol}^{-1}$ . The positive enthalpy of adsorption

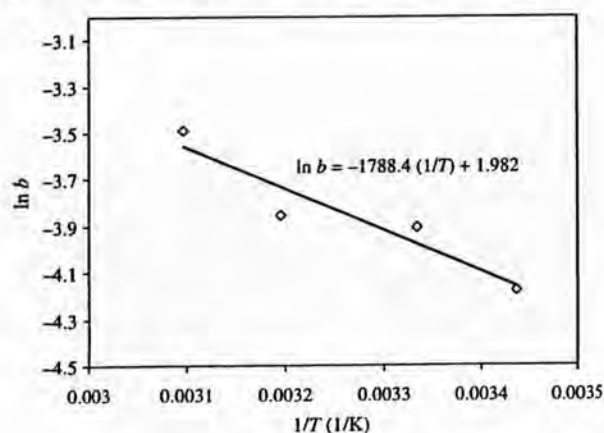


Fig. 7. Plot of  $\ln b$  versus  $1/T$  for Astrazon Blue FGRL for the determination of adsorption enthalpy.

Table 4  
Maximum sorption capacity of various types of basic dye by activated carbon and some natural adsorbents

Adsorbent	Adsorbate	$q_m$ ( $\text{mg g}^{-1}$ )	Reference
Activated carbon	Maxilon Scharz FBL-01	159.0	Meshko et al., 2001
Activated carbon	Maxilon Scharz FBL-01	33.70	Meshko et al., 2001
Activated carbon	Basic fuchsin	34.74	Gupta et al., 2003
Activated slag	Basic fuchsin	3.54	Gupta et al., 2003
Activated carbon	Astrazon Brilliant Red 4G	546.00–680.00	Faria et al., 2004
Palm fruit bunch particle	Basic Yellow (BY21)	327.57	Nassar and Magdy, 1997
Palm fruit bunch particle	Basic Red (BR22)	180.3	Nassar and Magdy, 1997
Palm fruit bunch particle	Basic Blue (BB3)	91.33	Nassar and Magdy, 1997
Raw date pits	Methylene Blue	80.29	Banat et al., 2003
Bagasse pith	Basic Blue 69 (BB69)	158.00	McKay et al., 1987
Bagasse pith	Basic Red 22 (BR22)	77.00	McKay et al., 1987
Giant duckweed	Methylene Blue	27.62–129.87	Waranusantigul et al., 2003
Macroalga <i>C. lentillifera</i>	Astrazon Blue FGRL	49.26	This study

indicated chemical adsorption. This suggested that the chemical bond between the *C. lentillifera* surface and the dye molecules could not be easily desorbed by physical means such as simply shaking or heating.

## 4. Conclusion

The experimental results showed that *Caulerpa lentillifera* could potentially be employed as a biosorbent in the removal of a basic dye, Astrazon Blue FGRL. The adsorption equilibrium and kinetic parameters such as the Langmuir and Freundlich constants, maximum capacity of adsorption, enthalpy of adsorption, and kinetic rate constants were also obtained from these experiments. These parameters could be used in the design of continuous flow experiments or scale-up batch experiments.

To illustrate the potential in the use of *C. lentillifera* in actual applications, a comparative evaluation of the adsorption capacities of various types of adsorbents for the sorption of basic dyes is provided in Table 4. Although this comparison shows that the adsorption capacity of the alga was not among the highest available, a relatively high uptake capacity of the dye could be obtained. This rendered the alga a promising biosorbent for color removal, especially from dye-containing effluent of the textile industry. In addition, *C. lentillifera* is freely available in large quantities, especially in closed loop shrimp farms.

The treatment method has, hence, emerged as a potentially economical means for the removal of basic dye. Moreover, the utilization of this alga for color removal from wastewater is also an attractive treatment alternative for the over-grown alga.

### Acknowledgements

This study was financially supported by the Royal Golden Jubilee Ph.D. Scholarship, the Thailand Research Fund (TRF) and the National Research Center for Environmental and Hazardous Waste Management (NRC-EHWM). The dye samples were provided by Dystar Thai Co., Ltd. and the *Caulerpa lentillifera* biomass was from Banchong Farm, Chachoengsao province, Thailand.

### References

- Aksu, Z., Tezer, S., 2000. Equilibrium and kinetic modeling of biosorption of Remazol Black B by *Rhizopus arrhizus* in a batch system: effect of temperature. *Process Biochem.* 36 (5), 431–439.
- Banat, F., Al-Asheh, S., Al-Makhadmeh, L., 2003. Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters. *Process Biochem.* 39 (2), 193–202.
- Crist, R.H., Oberholser, K., Shank, N., Nguyeh, M., 1981. Nature of bonding between metallic ions and algal cell walls. *Environ. Sci. Technol.* 15 (10), 1212–1217.
- Dogan, M., Alkan, M., Türkyilmaz, A., Özdemir, Y., 2004. Kinetics and mechanism of removal of methylene blue by adsorption onto perlite. *J. Hazard. Mater.* 109 (1–3), 141–148.
- Faria, P.C.C., Órfão, J.J.M., Pereira, M.F.R., 2004. Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries. *Water Res.* 38 (8), 2043–2052.
- Faust, S.D., Aly, O.M., 1987. *Adsorption Process for Water Treatment*. Butterworths, Boston.
- Freundlich, H.M.F., 1906. Über die adsorption in lösungen. *Z. Phys. Chem. (Leipzig)* 57A, 385–470.
- Garg, V.K., Kumar, R., Gupta, R., 2004. Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: a case study of *Prosopis cineraria*. *Dyes Pigments.* 62 (1), 1–10.
- Gupta, V.K., Ali, I., Suhas, Dinesh Mohan, 2003. Equilibrium uptake and sorption dynamics for the removal of a basic dye (basic red) using low-cost adsorbents. *J. Colloid Interface Sci.* 265 (2), 257–264.
- Ho, Y.S., 2003. Citation review of Lagergren kinetic rate equation on adsorption reactions. *Scientometrics* 59 (1), 171–177.
- Ho, Y.S., McKay, G., 2003. Pseudo-second-order model for sorption processes. *Process Biochem.* 34 (5), 451–465.
- Langmuir, I., 1916. The constitution and fundamental properties of solids and liquids. *J. Am. Chem. Soc.* 38 (11), 2221–2295.
- Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* 40 (9), 1361–1403.
- Lagergren, S., 1898. Zur Theorie der sogenannten adsorption gelöster stoffe. *Kungliga Svenska Vetenskapsakademiens. Handlingar, Band 24* (4).
- Lee, C.K., Low, K.S., Chow, S.W., 1996. Chrome sludge as an adsorbent for colour removal. *Environ. Technol.* 17 (9), 1023–1028.
- Lin, S.H., Lin, C.M., 1993. Treatment of textile waste effluent by ozonation and chemical coagulation. *Water Res.* 27 (12), 1743–1748.
- McKay, G., El Geundi, M., Nassar, M.M., 1987. Equilibrium studies during the removal of dyestuffs from aqueous solutions using bagasse pith. *Water Res.* 21 (12), 1513–1520.
- Meshko, V., Markovska, L., Mincheva, M., Rodrigues, A.E., 2001. Adsorption of basic dyes on granular activated carbon and natural zeolite. *Water Res.* 35 (14), 3357–3366.
- Namasivayam, C., Kanchana, N., 1992. Waste banana pith as adsorbent for color removal from Wastewaters. *Chemosphere* 25 (11), 1691–1705.
- Namasivayam, C., Kavitha, D., 2002. Removal of congo red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. *Dyes Pigments.* 54 (1), 47–58.
- Nassar, M.M., Magdy, Y.H., 1997. Removal of different basic dyes from aqueous solutions by adsorption on palm-fruit bunch particles. *Chem. Eng. J.* 66 (3), 223–226.
- Nigam, P., Armour, G., Banat, I.M., Singh, D., Marchant, R., 2000. Physical removal of textile dyes and solid state fermentation of dye adsorbed agricultural residues. *Bioresour. Technol.* 72 (3), 219–226.
- Pak, D., Chang, W., 1999. Decolorizing dye wastewater with low temperature catalytic oxidation. *Water Sci. Technol.* 40 (4), 115–121.
- Robinson, T., McMullan, G., Macchiant, R., Nigam, P., 2001. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresour. Technol.* 77 (3), 247–255.
- Robinson, T., Chandran, B., Nigam, P., 2002. Effect of pretreatments of three waste residues, wheat straw, corncobs and barley husks on dye adsorption. *Bioresour. Technol.* 85 (2), 119–124.
- Skoog, A.D., Leary, J.J., 1992. *Principle of Instrumental Analysis*. Saunders College Publishing, Florida.
- US EPA, 1996. Best management practice for pollution prevention in the textile industry. EPA/625/R-96/004, Ohio.
- Waranusantigul, P., Pokethitayook, P., Kruatrachue, M., Upatham, E.S., 2003. Kinetic of basic dye (methylene blue) biosorption by giant duckweed (*Spirodela polyrrhiza*). *Environ. Pollut.* 125 (3), 385–392.
- Weber, J.W., 1972. *Physicochemical Processes for Water Quality Control*. Wiley-Interscience, New York.
- Yesilada, O., Cing, S., Asma, D., 2002. Decolourization of the textile dye Astrazon Red FBL by *Funalia trogii* pellets. *Bioresour. Technol.* 81 (2), 155–157.
- Zollinger, H., 1987. *Colour Chemistry-Synthesis, Properties and Application of Organic Dyes and Pigments*. VCH, New York.



## High performance biosorbent (*Caulerpa lentillifera*) for basic dye removal

Khanidtha Marungrueng<sup>a</sup>, Prasert Pavasant<sup>b,\*</sup>

<sup>a</sup> National Research Center for Environmental and Hazardous Waste Management, Chulalongkorn University, Bangkok 10330, Thailand

<sup>b</sup> Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

Received 15 March 2006; received in revised form 12 June 2006; accepted 12 June 2006

Available online 22 August 2006

### Abstract

The sorptions of three basic dyes, Astrazon<sup>®</sup> Blue FGRL (AB), Astrazon<sup>®</sup> Red GTLN (AR), and methylene blue (MB) onto green macroalga *Caulerpa lentillifera* were investigated. The results were compared to the sorption performance of a commercial activated carbon (CARBON). The results revealed that the alga exhibited greater sorption capacities than activated carbon for the three basic dyes investigated in this work. The sorption process for all mixture systems (ALGA/AB, ALGA/AR, ALGA/MB, CARBON/AB, CARBON/AR, and CARBON/MB) obeyed the pseudo-second order kinetic model. *C. lentillifera* could more rapidly sequester AR when compared with activated carbon, but was more slowly in the sorption of AB. For the sorption of MB, both ALGA and CARBON seemed to have the same sorption rate. The sorption processes were initially controlled by both film and pore-diffusion, and only were limited by pore diffusion in the later stage. The isotherms followed Langmuir model which suggested that the sorption was monolayer coverage.

© 2006 Elsevier Ltd. All rights reserved.

**Keywords:** Wastewater; Textile dye; Decolorization; Langmuir; Pseudo-second order; Sorption kinetics

### 1. Introduction

Basic dyes are widely used in acrylic nylon and wool dyeing. The dye structures generally embody aromatic with various functional groups. The complex molecular structure often renders them recalcitrant. Some dyes have been reported to cause allergy, irritation, cancer, and even mutation in humans (Bhattacharyya and Sharma, 2004), and therefore the removal of dyes from waste streams before discharge to public water sources is of primary concern.

Sorption is generally regarded as an effective technique for the treatment of dye-containing wastewater. One of the most widely used sorbents is activated carbon which has relatively high sorption capacity for a wide variety of dyes (Choy et al., 1999; Robinson et al., 2001). Due to eco-

nomical reasons, several attempts have been made to find alternative sorbents particularly for the sorption of basic dyes. Examples of these biosorbents include orange peel (Namasivayam et al., 1996), palm fruit bunch (Nassar and Magdy, 1997), peat (Ho and McKay, 1998a), teak wood bark, cotton waste, rice husk (McKay et al., 1999), sugar cane dust (Khattri and Singh, 1999), bagasse fly ash (Gupta et al., 2000), and bagasse pith (McKay et al., 2003).

Recently, the unwanted agricultural by-product, i.e. green macroalga, *Caulerpa lentillifera*, was proven to be effective in removing basic dyes from the concocted waste stream (Marungrueng and Pavasant, 2006). This work then aimed to extend the basic knowledge on the application of this particular biosorbent on the sorption of a wider range of basic dyes, including the two widely used, commercial basic dyes: Astrazon<sup>®</sup> Blue FGRL and Astrazon<sup>®</sup> Red GTLN. In addition, the effectiveness of this biosorbent on the removal of basic dyes was compared with that of

\* Corresponding author. Tel.: +66 2 218 6870; fax: +66 2 218 6877.  
E-mail address: Prasert.p@chula.ac.th (P. Pavasant).

### Nomenclature

$b$	Langmuir constant ( $\text{Lmg}^{-1}$ )	$q_e$	equilibrium dye concentration per unit mass of sorbent ( $\text{mg g}^{-1}$ )
$C_e$	dye concentration in liquid phase at equilibrium ( $\text{mg g}^{-1}$ )	$q_{e,\text{exp}}$	equilibrium dye concentration per unit mass of sorbent obtained from experiments ( $\text{mg g}^{-1}$ )
$D$	effective diffusivity of solutes within particle ( $\text{m}^2 \text{min}^{-1}$ )	$q_m$	maximum amount of dye sorbed per unit mass of sorbent calculated from Langmuir plots ( $\text{mg g}^{-1}$ )
$k_1$	sorption rate constants for first order kinetic equation ( $\text{min}^{-1}$ )	$q_t$	amount of dye sorbed per unit mass of sorbent at time $t$ ( $\text{mg g}^{-1}$ )
$k_2$	sorption rate constants for second order kinetic equation ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$R^2$	linear regression coefficient (–)
$K_f$	Freundlich constant ( $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$ )	$r_p$	particle radius (m)
$k_i$	intra-particle diffusion rate constant ( $\text{mg min}^{0.5} \text{g}^{-1}$ )	$t$	time (min)
$1/n$	Freundlich exponent (unitless)	$t^{0.5}$	half sorption time of dye ( $\text{min}^{0.5}$ )

activated carbon, the commonly used sorbent, using 'methylene blue' as a common dye for comparative evaluation.

## 2. Methods

### 2.1. Basic dyes

The modeled basic dyes examined in this work were: Astrazon® Blue FGRL (AB), Astrazon® Red GTLN (AR), and methylene blue (MB). Astrazon® Blue FGRL consists of two main components: C.I. basic blue 159 and C.I. basic blue 3. The ratio of the two components is approximately 5:1 by weight, respectively. Astrazon® Red GTLN also consists of two main components, which are C.I. basic red 18:1 and C.I. basic yellow 28. The ratio of the two components is approximately 40:1 by weight, respectively. The two commercial dyes were supplied by Dystar Thai Co., Ltd. Methylene blue (Sharlau Chemie), on the other hand, is a pure dye, generally known as C.I. basic blue 9.

### 2.2. Sorbent preparation

*Caulerpa lentillifera* was collected from Banchong Farm, Chachoengsao province, Thailand. After being washed with deionized water, the alga was dried at 80 °C for 12 h. Activated carbon (Union Chemical®) used in this experiment was commercial grade. Its technical characteristics as reported in the product certificate of analysis were: moisture content 4.9%, ash content 2.3%, apparent density 0.47  $\text{g cm}^{-3}$ , and iodine number 1150  $\text{mg g}^{-1}$ . Both algal sorbent and activated carbon were stored in the desiccator before use.

### 2.3. Sorbent characterization

The dried alga was ground to the particle size range of less than 20  $\mu\text{m}$  and then mixed with 1000 mg KBr in the sample disk. The functional groups located on algal surface

were specified using Fourier Transform Infrared Spectrophotometer (FTIR), Perkin Elmer, Model 1760X. Surface characteristics of the algal sample were analyzed by BET method using Surface Area Analyzer (Quantachrome, Autosorb-1).

### 2.4. Sorption experiments

Sorption experiments were carried out in a batch process by using synthetic aqueous dye solution. The experiments could be categorized into six groups: (i) sorption of Astrazon® Blue FGRL by *C. lentillifera* or denoted as "ALGA/AB", (ii) Astrazon® Red GTLN by *C. lentillifera* (ALGA/AR), (iii) methylene blue by *C. lentillifera* (ALGA/MB), (iv) Astrazon® Blue FGRL by activated carbon (CARBON/AB), (v) Astrazon® Red GTLN by activated carbon (CARBON/AR), and (vi) methylene blue by activated carbon (CARBON/MB). The sorption isotherms at 25 °C were examined by submerging the sorbent (with the weight in the range of 0.5–2.0 g) into 30 ml of synthetic dye solution for one hour. The mixture was gently shaken at 130 rpm on a rotary shaker (GFL 3017). The sorption kinetics was investigated using similar sorption technique where 0.5 g of dry *C. lentillifera* was mixed in synthetic dye solutions. The pH during the experiments was controlled at  $7 \pm 0.5$  using 0.1 N HCl and 0.1 N NaOH. In this case, samples were collected to analyze for the residue dye under a certain time interval using spectrophotometer (Spectronic® UV/VIS Helios Alpha spectrophotometer operated with Vision32 software-v1.25). The measurements were performed at the wavelengths of 576, 512 and 665 nm for AB, AR and MB, respectively.

## 3. Results and discussions

### 3.1. Sorbent characterizations

The possible functional groups on algal surface were shown in Table 1 which illustrated that the most abundant

Table 1  
Functional groups in dried *C. lentillifera*

Functional group	Standard Wavenumber (Skoog and Leary, 1992) (cm <sup>-1</sup> )	Wavenumber from the results (cm <sup>-1</sup> )	Relative quantity <sup>a</sup>
Hydroxyl; O-H	3250–3700	3200–3600	1
Carboxyl; COOH	2400–3300	3200–3600	1
Amine; NH <sub>2</sub>	3300–3500	3200–3600	1
C-O	1050–1300	1000–1200	2
Sulfonyl; S=O	1040–1200	1000–1200	2
Carbonyl; C=O	1670–1780	1600–1750	3
S-O	550–650	500	4
Alkyl; C-H	Carboxylic acid: 2500–3100 Alcohol: 3400–3640	2900–3000	5

<sup>a</sup> The quantity in the order from large to small (1 is the most abundant and 5 is the least).

function groups included carboxyl and amine. C-O and sulfonyl were second most abundant followed by carbonyl, S-O, and alkyl, respectively. BET analysis demonstrated that the algal sorbent had a specific surface area of 4.94 m<sup>2</sup>g<sup>-1</sup>, pore specific volume of 0.016 cm<sup>3</sup>g<sup>-1</sup> with a median pore width of 85.91 Å which represented mesopore structure (Rouquerol et al., 1999).

### 3.2. Sorption kinetics

The sorption kinetics of dye removal by *C. lentillifera* and activated carbon were investigated. The equilibriums were reached within one hour for all sorption systems, i.e. the equilibrium times were 10 min for the ALGA/AB system, 30 min for ALGA/AR, 30 min for ALGA/MB, 10 min for CARBON/AB, 60 min for CARBON/AR, and 30 min for CARBON/MB. AR was shown to be more easily sequestered by ALGA than by CARBON, as it only required 30 min to reach equilibrium for ALGA whereas the equilibrium time for CARBON was as long as 60 min. This finding suggested that the functional groups on algal surface could have more affinity with AR than activated carbon. Both sorbents seemed to have the similar affinities for AB and MB. The rates of sorption for each sorption system were also examined by applying the results with kinetic models.

Three kinetic models, pseudo-first order, pseudo-second order, and intra-particle diffusion models were employed to

determine the kinetic nature of each sorption system. Pseudo-first order kinetic model (Lagergren, 1898) has been widely used to predict the dye sorption kinetics. This can be expressed in a mathematical form as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t). \quad (1)$$

The integrated form of Eq. (1) with initial/final conditions of:  $q_t = 0$  at  $t = 0$ , and  $q_t = q_e$  at  $t = t$  is

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t, \quad (2)$$

where  $q_e$  is the amount of dye uptaken at equilibrium time (mg g<sup>-1</sup>),  $q_t$  the amount of dye uptaken at time  $t$  (mg g<sup>-1</sup>),  $t$  time (min) and  $k_1$  the rate constant for the pseudo-first order model (min<sup>-1</sup>).

The pseudo-first order rate constant,  $k_1$ , can be calculated from the plot of  $\log(q_e - q_t)$  versus time  $t$ . The resulting  $k_1$  value and  $R^2$  for each sorption system are shown in Table 2. A relatively low correlation coefficient implied that this first order model was not appropriate in describing such relationships.

The pseudo-second order kinetic model derived by Ho and McKay (1999), on the other hand, has been proven to be suitable for several sorption systems (Ho and McKay, 1998b,c; Fu and Viraraghavan, 2000; Banat et al., 2003). This takes the following mathematical form

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2. \quad (3)$$

Integrating Eq. (3) with initial/final conditions of:  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_e$  gives

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad (4)$$

where  $k_2$  is the pseudo-second order rate constant (g mg<sup>-1</sup> min<sup>-1</sup>).

The linear plots of  $t/q_t$  versus  $t$  for the pseudo-second order in Eq. (4) were obtained for all sorption systems as shown in Fig. 1.  $q_e$  and  $k_2$  can be directly determined from the slope and intercept of the plot. The model parameters are also shown in Table 1. The  $q_e$  values calculated from the pseudo-second order are in good agreement with the experimental data,  $q_{e,exp}$ , and the extremely high  $R^2$  (>0.999) for all sorption systems indicated that the sorption

Table 2  
Comparison of kinetic parameters for the sorption of basic dyes onto *C. lentillifera* and activated carbon

Sorption system	$q_{e,exp}$ (mg g <sup>-1</sup> )	First order		Pseudo-second order		
		$k_1$ (min <sup>-1</sup> )	$R^2$	$q_{e,2}$ (mg g <sup>-1</sup> )	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$R^2$
ALGA/AB	4.55	$(18.3 \pm 1.8) \times 10^{-2}$	0.8266	$4.57 \pm 0.34$	$(25.3 \pm 1.8) \times 10^{-2}$	1
CARBON/AB	3.67	$(36.4 \pm 3.8) \times 10^{-2}$	0.7121	$3.68 \pm 0.42$	$(74.7 \pm 8.3) \times 10^{-2}$	1
ALGA/AR	4.55	$(33.8 \pm 3.4) \times 10^{-2}$	0.8428	$4.55 \pm 0.33$	$(36.1 \pm 3.5) \times 10^{-2}$	1
CARBON/AR	4.61	$(16.4 \pm 1.8) \times 10^{-2}$	0.7671	$4.65 \pm 0.40$	$(18.8 \pm 2.3) \times 10^{-2}$	0.9999
ALGA/MB	4.70	$(10.2 \pm 1.2) \times 10^{-2}$	0.9618	$4.73 \pm 0.39$	$(21.3 \pm 1.9) \times 10^{-2}$	1
CARBON/MB	4.80	$(4.39 \pm 4.8) \times 10^{-2}$	0.8850	$4.88 \pm 0.47$	$(21.4 \pm 2.2) \times 10^{-2}$	0.9998

Confidential interval of the data by  $t$ -test of 95% ( $\alpha = 0.05$ ).

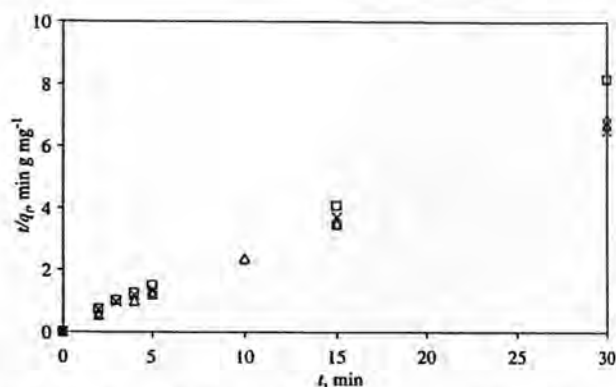


Fig. 1. Pseudo-second order kinetics basic dyes on dried *C. lentillifera* and activated carbon (◇ ALGA/AB, △ ALGA/AR, ○ ALGA/MB, □ CARBON/AB, × CARBON/AR, + CARBON/MB).

kinetics could be best described by this model. This finding supported the assumption of the pseudo-second order model that the sorption process was due to chemisorption (Ho, 2003). In this case, chemical sorption could have occurred by the interaction between polar functional groups on the sorbent surface and dyes. Similar phenomena have been observed in the biosorption of Remazol Black B on biomass (Aksu and Tezer, 2000), the sorption of Congo Red on activated carbon (Namasivayam and Kavitha, 2002) and Methylene Blue on perlite (Doğan et al., 2004). In order to understand the sorption mechanism, the functional groups on the algal surface were specified using FTIR technique. Table 1 displays possible functional groups on the algal surface, including hydroxyl, carbonyl, amine, sulfonyl, carbonyl, and alkyl groups. These functional groups can act as chemical binding agents. Carboxyl, hydroxyl, and sulfonyl groups can dissociate and become negative charge. That means these functional groups could attract the positive charge functional groups on dye structures such as quaternary ammonium ion ( $\text{NR}_4^+$ ) and nitronium ion ( $\text{NO}_2^+$ ), and this is called "Negative sorption" which is the sorption of the positive species by negative sorption sites (Volesky, 1990). The second order rate constants for the sorption of methylene blue onto *C. lentillifera* took the value of  $0.21 \text{ gm}^{-1} \text{ min}^{-1}$ . This was relatively high with respect to the rate constants for other biosorbents, e.g.  $k_2 = 0.087 \text{ gm}^{-1} \text{ min}^{-1}$  for the sorption of methylene blue on perlite (Acemioğlu, 2005), or  $= 0.0137 \text{ gm}^{-1} \text{ min}^{-1}$  for the sorption of methylene blue on rice husk (Vadivelan and Vasanth Kumar, 2005). High  $k_2$  suggested that the basic dyes could be rapidly uptaken by the algal functional groups, resulting in the system quickly reaching equilibrium as reported earlier.

It is interesting to note that the second order rate constants for the sorption of methylene blue for the two sorbents were in the same range. Conventionally, this implies that the two sorbents could be regarded as equally effective in the sorption of dyes. However, activated carbon gave a higher second order rate constant for the sorption of AB than *C. lentillifera*, whilst *C. lentillifera* exhibited a

higher second order rate constant for AR. Generally,  $k_2$  acquired from the pseudo-second order model implies the rate of color removal. Hence, the  $k_2$  results indicated that *C. lentillifera* could more rapidly sequester AR when compared with activated carbon, but was more slowly in the sorption of AB. With respect to the sorption of MB, both ALGA and CARBON seemed to have the same sorption characteristics, i.e. the same sorption capacity and the same equilibrium time. The finding illustrated that methylene blue might not be a good representative of sorption efficiency as it does not reflect the actual sorption capacity of the sorbent for other types of dyes.

### 3.3. The rate limiting step

The analysis for the rate limiting step is an important step in the investigation of sorption processes (Sarkar et al., 2003). Generally, the sorption process can be described by three consecutive steps, starting with the liquid film diffusion, internal diffusion, and sorption of solute on the interior surfaces of the pores and capillaries space of the sorbent (Vadivelan and Vasanth Kumar, 2005). Among these three steps, the last step is often relatively fast and thus is not considered as a rate determining step (Crank, 1956). The sorption of basic dyes onto both activated carbon and *C. lentillifera* should therefore be governed by film diffusion process and/or intra-particle diffusion.

Intra-particle diffusion model developed by Weber and Morris (1963) described the process in which the rate limiting step was not external mass transfer. The rate of intra-particle diffusion is a function of  $t^{0.5}$  and can be defined as follows:

$$q_t = f\left(\frac{Dt}{r_p^2}\right)^{0.5} = k_i t^{0.5}, \quad (5)$$

where  $r_p$  is particle radius (m),  $D$  the effective diffusivity of solutes within particle ( $\text{m}^2 \text{ min}^{-1}$ ),  $k_i$  intra-particle diffusion

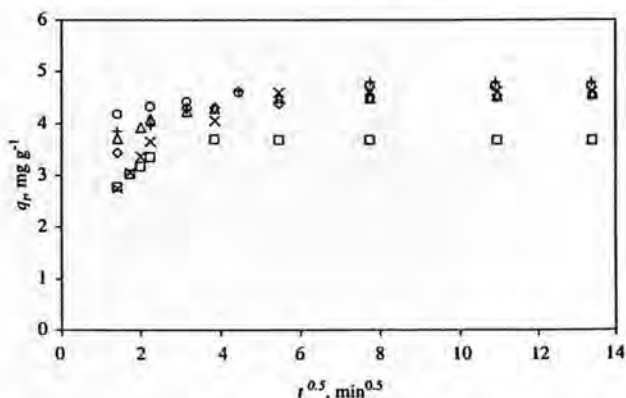


Fig. 2. Intra-particle diffusion plots for the sorption of basic dyes on dried *C. lentillifera* and activated carbon (◇ ALGA/AB, △ ALGA/AR, ○ ALGA/MB, □ CARBON/AB, × CARBON/AR, + CARBON/MB).



rate constant ( $\text{mg g}^{-1} \text{mol}^{-0.5}$ ), and  $t$  time (min). The plots of  $t^{0.5}$  versus  $q_t$  are shown in Fig. 2. It was noticed that all plots showed multi-linearity where a steeper curve at the beginning of experiment implied a faster sorption than the sorption at the later stage. In other words, during the initial period, the sorption could take place more easily as the sorbate could move at a faster speed and not restricted by the difference in the concentration levels. In this case, both film and pore (intra-particle) diffusions were rate limiting steps. The later portion of the curve increased at a much slower rate and this suggested the situation where the concentration of sorbate inside the particle was already quite high, exhibiting a smaller concentration gradient which restricted the movement of the sorbate. Hence, at later stage, intra-particle diffusion was considered to be the main rate limiting step.

### 3.4. Sorption isotherms

The sorption data were arranged according to the Langmuir (1916) and Freundlich (1906) isotherm forms. These isotherms are as expressed in Eqs. (6) and (7).

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (6)$$

$$q_e = K_f C_e^{1/n}, \quad (7)$$

where  $q_m$  represents the maximum amount of dye uptaken per unit mass of the sorbent calculated from Langmuir plots ( $\text{mg g}^{-1}$ ),  $b$  Langmuir constant ( $\text{l mg}^{-1}$ ),  $C_e$  equilibrium concentration of the dye in the solution ( $\text{mg l}^{-1}$ ),  $K_f$  Freundlich constant ( $\text{mg}^{1-1/n} \text{l}^{1/n} \text{g}^{-1}$ ),  $1/n$  Freundlich exponent (unitless). To facilitate parameter fittings, all isotherm equations were linearized, where Eqs. (6) and (7) become:

$$\frac{1}{q_e} = \frac{1}{q_m} + \left( \frac{1}{b q_m} \right) \left( \frac{1}{C_e} \right) \quad (8)$$

$$\ln q_e = \ln K_f + \left( \frac{1}{n} \right) \ln C_e. \quad (9)$$

Parameter fitting revealed that experimental data could not be arranged in the linear form according to Eq. (9). Hence, Freundlich isotherm was considered not appropriate for describing the sorption nature of all six systems (results not shown here). On the other hand, a straight line could be well observed between  $1/q_e$  and  $1/C_e$  indicating that experimental data followed Langmuir model (Fig. 3). This finding suggested that the sorption of dyes on *C. lentillifera* and activated carbon was monolayer coverage.

Isotherm parameters are tabulated in Table 3. For AB and AR, the sorption onto activated carbon gave higher Langmuir constant,  $b$ , which means higher affinity than those of *C. lentillifera*. The parameter  $b$  of ALGA/MB was higher than that of CARBON/MB, indicating that methylene blue had more affinity with *C. lentillifera*. The highest  $b$  of  $0.107 \text{ l mg}^{-1}$  was obtained from the sorption of AB onto activated carbon (CARBON/AB). However, a

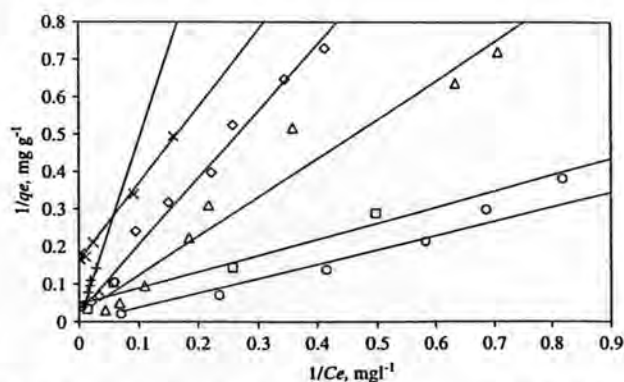


Fig. 3. Langmuir plots for the six sorption systems ( $\diamond$  ALGA/AB,  $\Delta$  ALGA/AR,  $\circ$  ALGA/MB,  $\square$  CARBON/AB,  $\times$  CARBON/AR,  $+$  CARBON/MB).

Table 3  
Langmuir parameters of the sorption of basic dyes onto *C. lentillifera* and activated carbon

Sorption System	Langmuir isotherm parameters		$R^2$
	$q_m$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{l mg}^{-1}$ )	
ALGA/AB	$38.9 \pm 3.4$	$(1.44 \pm 0.23) \times 10^{-2}$	0.9873
CARBON/AB	$21.6 \pm 2.4$	$(1.07 \pm 0.12) \times 10^{-1}$	0.9797
ALGA/AR	$47.6 \pm 4.2$	$(2.02 \pm 0.18) \times 10^{-2}$	0.9477
CARBON/AR	$6.20 \pm 0.92$	$(7.86 \pm 1.2) \times 10^{-2}$	0.9930
ALGA/MB	$417 \pm 19$	$(6.29 \pm 0.29) \times 10^{-3}$	0.9581
CARBON/MB	$238 \pm 12$	$(8.82 \pm 0.44) \times 10^{-4}$	0.9703

Confidential interval of the data by  $t$ -test of 95% ( $\alpha = 0.05$ ).

Table 4  
Comparison of sorption capacity of methylene blue onto various sorbents

Sorbent	Temperature ( $^{\circ}\text{C}$ )	$q_{\text{max}}$ ( $\text{mg g}^{-1}$ )	References
Teak wood bark	20	915	McKay et al., 1999
<i>C. lentillifera</i>	25	417	This study
Rice husk	20	312	McKay et al., 1999
Cotton waste	20	278	McKay et al., 1999
Activated carbon	25	238	This study
Giant duckweed	25	145	Waranusantigul et al., 2003
Activated tyres	–	130	Saniz-Diaz and Griffiths, 2000
Activated sewage char	–	120	Saniz-Diaz and Griffiths, 2000
Rice husk	32	40.6	Vadivelan and Vasanth Kumar, 2005
Raw date pits	20	80.3	Robinson et al., 2001
Amorphous silica	–	26.5	Woodlard et al., 2002
Zeolite	–	12.7	Woodlard et al., 2002

higher  $q_m$  for *C. lentillifera* suggested that the alga had higher sorption capacity than activated carbon. For all three dyes, *C. lentillifera* gave higher  $q_m$  than activated carbon where the highest  $q_m$  of  $417 \text{ mg g}^{-1}$  was achieved for the sorption of methylene blue on *C. lentillifera* (ALGA/MB).

#### 4. Conclusion

Maximum sorption capacity ( $q_m$ ) obtained from the sorption of MB onto *C. lentillifera* was  $417 \text{ mg g}^{-1}$  which was relatively high in comparison with the previous records as summarized in Table 4. Sorption behaviors of the six systems were compared in order to give comparative evaluation where the sorption capacity of the alga was proven to be superior to that of activated carbon. Moreover, the equilibrium times of the algal systems were found to be shorter and this rendered the alga a potential biosorbent for color removal.

#### Acknowledgements

This study was financially supported by the Royal Golden Jubilee Ph.D. Scholarship, the Thailand Research Fund (TRF). The dye samples were provided by Dystar Thai Co., Ltd. *Caulerpa lentillifera* biomass was from Banchong Farm, Chachoengsao province, Thailand.

#### References

- Acemiođiu, B., 2005. Batch kinetic study of sorption of methylene blue by perlite. *Chem. Eng. J.* 106 (1), 73–81.
- Aksu, Z., Tezer, S., 2000. Equilibrium and kinetic modeling of biosorption of Remazol Black B by *Rhizopus arrhizus* in a batch system: effect of temperature. *Process Biochem.* 35 (5), 431–439.
- Banat, F., Al-ashah, S., Al-Makhadmeh, L., 2003. Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters. *Process Biochem.* 39 (2), 193–202.
- Bhattacharyya, K.G., Sharma, A., 2004. *Azadirachta indica* leaf powder as an effective biosorbent for dyes: a case study with aqueous Congo Red solutions. *J. Environ. Manage.* 71 (3), 217–229.
- Choy, K.K.H., McKay, G., Porter, J.F., 1999. Sorption of acid dyes from effluents using activated carbon. *Resour. Conserv. Recycl.* 27 (1), 57–71.
- Crank, J., 1956. *The Mathematics of Diffusion*. Clarendon Press, Oxford.
- Doğan, M., Alkan, M., Turkyilmaz, Ozdemir, Y., 2004. Kinetics and mechanism of removal of methylene blue by adsorption onto perlite. *J. Hazard. Mater.* 109 (1–3), 141–148.
- Freundlich, H.M.F., 1906. Über die adsorption in Lösungen. *Zeitschrift für Physikalische Chemie (Leipzig)* 57A, 385–470.
- Fu, Y.Z., Viraraghavan, T., 2000. Removal of a dye from an aqueous solution by the fungus *Aspergillus niger*. *Water Qual. Res. J. Can.* 35 (1), 95–111.
- Gupta, V.K., Mohan, D., Sharma, S., Sharma, M., 2000. Removal of Basic dyes (Rhodamine B and Methylene Blue) from aqueous solution using bagasse fly ash. *Sep. Sci. Technol.* 35 (13), 2097–2113.
- Ho, Y.S., 2003. Removal of copper ions from aqueous solution by tree fern. *Water Res.* 37 (10), 2323–2330.
- Ho, Y.S., McKay, G., 1998a. Sorption of dye from aqueous solution by peat. *Chem. Eng. J.* 70 (2), 115–124.
- Ho, Y.S., McKay, G., 1998b. Kinetic model for the sorption of dye from aqueous solution by wood. *Process Saf. Environ. Prot.* 76 (B2), 183–191.
- Ho, Y.S., McKay, G., 1998c. The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat. *Can. J. Chem. Eng.* 76 (4), 822–827.
- Ho, Y.S., McKay, G., 1999. Pseudo-second order model for sorption processes. *Process Biochem.* 34 (5), 451–465.
- Khattari, S.D., Singh, M.K., 1999. Colour removal from dye wastewater using sugar cane dust as an adsorbent. *Adsorp. Sci. Technol.* 17 (4), 269–282.
- Lagergren, S., 1898. Zur Theorie der sogenannten adsorption gelöster stoffe. *Kungliga Svenska Vetenskapsakademiens. Handlingar Band 24* (4).
- Langmuir, I., 1916. The constitution and fundamental properties of solids and liquids. *J. Amer. Chem. Soc.* 38 (11), 2221–2295.
- Marungrueng, K., Pavasant, P., 2006. Removal of basic dye (Astrazon Blue FGRL) using macroalga *Caulerpa lentillifera*. *J. Environ. Manage.* 78 (3), 268–274.
- McKay, G., Porter, J.F., Prasad, G.R., 1999. The removal of dye colours from aqueous solutions by adsorption on low-cost materials. *Water, Air, Soil Pollut.* 114 (3–4), 423–438.
- McKay, G., El-Geundi, M., Nassar, M.M., 2003. Equilibrium studies during the removal of dyestuffs from aqueous solutions using bagasse pith. *Water Res.* 21 (12), 1513–1520.
- Namasivayam, C., Kavitha, D., 2002. Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. *Dyes Pigments* 54 (1), 47–58.
- Namasivayam, C., Muniasamy, N., Gayatri, K., Rani, M., Ranganathan, K., 1996. Removal of dye from aqueous solutions by cellulosic waste orange peel. *Bioresour. Technol.* 57 (1), 37–43.
- Nassar, M.M., Magdy, Y.H., 1997. Removal of different basic dyes from aqueous solution by adsorption on palm-fruit bunch particles. *Chem. Eng. J.* 66 (3), 223–226.
- Robinson, T., McMullan, G., Marchant, R., Nigam, P., 2001. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresour. Technol.* 77 (3), 247–255.
- Rouquerol, F., Rouquerol, J., Sing, K., 1999. *Adsorption by powders and porous solids*. Academic Press, San Diego, Chapter 1, p. 1.
- Saniz-Diaz, C.I., Griffiths, A.J., 2000. Activated carbon from solid wastes using a pilot-scale batch flaming pyrolyser. *Fuel* 79 (15), 1863–1871.
- Sarkar, M., Acharya, P.K., Battacharya, B., 2003. Modeling the adsorption kinetics of some priority organic pollutants in water from diffusion and activation energy parameters. *J. Colloid Interface Sci.* 266 (1), 28–32.
- Skoog, D., Leary, J., 1992. *Principle of Instrumental Analysis*, fourth ed. Saunders College Publishing, Fort Worth.
- Vadivelan, V., Vasanth Kumar, K., 2005. Equilibrium, kinetics, mechanism and process design for the sorption of methylene blue onto rice husk. *J. Colloid Interface Sci.* 286 (1), 90–100.
- Volesky, B., 1990. *Biosorption of heavy metal*. CRC Press, Boston.
- Waranusantigul, P., Pokethitiyook, P., Kruatrachue, M., Upatham, E.S., 2003. Kinetic of basic dye (methylene blue) biosorption by giant duckweed (*Spirodela polyrrhiza*). *Environ. Pollut.* 125 (3), 385–392.
- Weber, W.J., Morris, J.C., 1963. Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div.* 89 (SA2), 31–39.
- Woodlard, C.D., Strong, J., Erasmus, C.R., 2002. Evaluation of the use of modified coal ash as a potential sorbent for organic waste streams. *Appl. Geochem.* 17 (8), 1159–1164.

## BIOGRAPHY

Born in 1980 into a merchant family in Samuthsakorn province, Khanidtha (Marungrueng) Meevasana started her first school at a local primary school in Kratumban District, Samuthsakorn. In 1997, she continued her study at Department of Biochemistry, Faculty of Science, Chulalongkorn University. After spending 4 years in Biochemistry department, she changed her interest to the environmental field. Khanidtha next went to Post-graduated program in Environmental and Hazardous Waste Management, graduated school in the same university. During Ph.D., she was granted a Royal Golden Jubilee Ph.D. scholarship from Thailand Research Fund and joined the 13<sup>th</sup> Regional Symposium on Chemical Engineering at Nanyang Technological University, Singapore. In 2007, right before she achieved her Ph.D. degree, she married Worawat Meevasana, a PhD candidate in Physics department, Standford University, and changed her Family name to Meevasana.