

利用廢棄魚鱗取代活性碳作為去除染整廢水色度之吸附劑可行性研究

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摘要

吳郭魚為台灣常見重要魚種，廢棄魚鱗每年產量大約高達九萬噸左右。因此，促使了由工業或漁業產物的殘餘物中獲得以魚鱗作為吸附劑。本研究以吳郭魚魚鱗作為吸附劑來去除Reactive Red 198 (R-R 198) 水溶液之染料。另外，我們將探討吳郭魚魚鱗其界達電位 (zeta potential)、不同染料去除色度和吸附染料之全波長，並且在魚鱗去除色度中來研究pH值、溫度和吸附劑量之影響，而以動力學研究來解析染料去除。此結果顯示染料去除百分比會隨著初始染料濃度的降低而增加，且隨著吸附劑使用量的增加而增加。此外，等溫吸附模式藉由Freundlich、Dubnin-Radushkevich、Langmuir、Temkin和Redlich-Peterson等溫線方程式來使用其相關係數，並分析五種不同誤差函數。結果發現Langmuir方程式為最適合代表染料R-R198來吸附吳郭魚魚鱗之平衡數據。

關鍵詞：魚鱗、染料、吸附劑、色度去除、動力學

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參考文獻

- 1.王怡敦。2003。礦物組成對燃煤飛灰去除水中銅離子之影響:27-29。嘉南藥理科技大學。嘉義,台灣。
- 2.王明光 譯。2000。環境土壤化學,初版。第127-179頁。國立編譯館。台北,台灣。
- 3.宋欣真和鄭仁川。1994。台灣地區染整業廢水污染防治現況。工業污染防治 49:27-46。
- 4.林育丞。2002。燃煤底灰應用於污染去除之研究:78-82。逢甲大學碩士論文。台中,台灣。
- 5.染整顧問服務中心。1997。染色工業之廢水處理(下)。染化雜誌 142:37-43。
- 6.孫嘉福、李孫榮、楊英賢和廖文彬。1997。燃煤灰渣去除水中鋅離子可行性之研究。中國環境工程學刊7:309-317。
- 7.許平和。1995。利用廢棄物去除無機性惡臭氣體(硫化氫)之可行性研究:16-24。逢甲大學碩士論文。台中,台灣。
- 8.章裕民。1995。環境工程化學,初版。文京書局。台北,台灣。
- 9.黃正義。1988。空氣污染污染源與防治。第302-322頁。淑馨出版社。台北,台灣。
- 10.楊萬發。1986。染整工廠廢水處理污染防治。工業污染防治技術手冊之二。經濟部工業污染防治技術服務團,財團法人中國技術服務社編印。
- 11.葉明和。1989。單元操作。第943-973頁。三民書局印行。台北,台灣。
- 12.潘建呈。1999。活性白土、蒙特土與活性碳對鹽基性染料吸附之研究:23-27。台灣科技大學化學工程所碩士論文。台北,台灣。
- 13.盧廷藏。2001。燃油飛灰中未燃碳活化行為之研究:14-15。成功大學資源工程研究所碩士論文。台南,台灣。
- 14.Acemioglu, B. 2004. Adsorption of Congo red from aqueous solution onto calcium-rich fly ash. *Journal of Colloid and Interface Science* 274:371-379.
- 15.Aharoni, C., Sideman, S. and Hoffer, E. 1979. Adsorption of phosphate ions by collodion-coated alumina. *Journal of Chemical Technology and Biotechnology* 29:404- 412.
- 16.Al-Degs, Y., Khraisheh, M. A. M., Allen, S. J. and Ahmad, M. N. A. 2001. Sorption behavior of cationic and anionic dyes from aqueous solution on different types of activated carbons. *Separation Science and Technology* 36: 91- 102.
- 17.Allen, S. J. 1987. Equilibrium adsorption isotherms for peat. *Fuel* 66:1171-1176.
- 18.Allen, S. J., McKay, G. and Khader, K. Y. H. 1989. Intraparticle diffusion of a basic dye during adsorption onto sphagnum peat. *Environmental Pollution* 56:39-50.
- 19.Al-Qodah, Z. 2000. Adsorption of dyes using shale oil ash. *Water research* 34:4295-4303.
- 20.Anliker, A. 1979. Ecotoxicology of dyestuffs-A joint effort by industry. *Ecotoxicology and Environmental Safety* 3:59-74.
- 21.Arslan, I., Balcioglu, I. A. and Tuhkanen, T. 1999. Oxidative treatment of simulated dye house effluent by UV and near UV light assisted Fenton's reagent. *Chemosphere* 39:2767-2783.
- 22.Asfour, H. M., I-Geundi, M. S., Fadali, O. A. and Nassar, M. M. 1985. Colour removal from textile effluents using hardwood sawdust as an adsorbent. *Journal of Chemical Technology and Biotechnology* 35:28-35.
- 23.Ayala, J., Blanco, F., Carcia, P., Rodriguez, P. and Sancho, J. 1998. Asturian fly ash as a heavy metals removal materials. *Fuel* 77:1147-1154.
- 24.Banerjee, K., Cheremisinoff, P. N. and Cheng, L. S. 1997. Adsorption kinetics of O-Xylene by fly ash. *Water Research* 31:249-261.
- 25.Banerjee, K., Cheremisinoff, P. N. and Cheng, S. L. 1995. Sorption of organic contaminants by fly ash in a single solute system. *Environmental Science and Technology* 29:2243-2251.
- 26.Besseau, L., and Bouligand, Y. 1998. The twisted collagen network of the box-fish scutes. *Tissue and Cell* 30:251-260.
- 27.Bertin, L. 1944. Modifications proposées dans la nomenclature des écailles et des nageoires. *Bull. Soc. Zool. Fr.* 69:198-202.
- 28.Carliell, C. M., Barclay, S. J. and Buckley, C. A. 1996. Treatment of exhausted reactive dye bath effluent using anaerobic digestion: Laboratory and full-scale trials. *Water SA* 22:225-233.
- 29.Chen, K. C., Huang, W. T., Wu, J. Y. and Huang, J. Y. 1999. Microbial decolorization of azo dyes by *Proteus mirabilis*. *Journal of Industrial Microbiology and Biotechnology* 23:686-690.
- 30.Chung, K. T and Stevens, S. E. 1993. Degradation of azo dyes by environmental microorganisms and helminths. *Environmental Toxicology and Chemistry* 12:2121-2132.
- 31.Chung, K. T., Fulk, G. E. and Andrews, A. W. 1981. Mutagenicity test of some commonly used dyes. *Applied and Environmental Microbiology* 42:641-648.
- 32.Cooper, C. D. and Alley, F. C. 1992. Air pollution control: A design approach. p. 343-372. Centralbook, Taipei, Taiwan.
- 33.Cripps, C., Bumpus, J. A. and Aust, S. D. 1990. Biodegradation of azo and heterocyclic dyes by *phanerochaete chrysosporium*, *Applied and Environmental Microbiology* 56:1114-1118.
- 34.Delee, W., O-Neil, C., Hawkes, F. R. and Pinheiro, H. M. 1998. Anaerobic treatment of textile effluents: a review. *Journal of Chemical Technology and Biotechnology* 73:323-335.
- 35.Dogan, M. and Alkan, M. 2003. Adsorption kinetics of methyl violet onto perlite. *Chemosphere* 50:517-528.
- 36.Fu, Y. and Viraraghavan, T. 2002. Removal of Congo Red from an aqueous solution by fungus *Aspergillus niger*. *Advances in Environmental Research*, 7 (1), 239- 247.
- 37.Goss, K. U. and Schwarzenbach, R. P. 2002. Adsorption of a diverse set of organic vapors on quartz, CaCO₃, and Al₂O₃ at different relative humidities. *Journal of Colloid and Interface Science* 252:31-41.
- 38.Guo, Y., Yang, S., Fu, W., Qi, J., Li, R., Wang, Z. and Xu, H. 2003. Adsorption of malachite green on micro- and mesoporous rice husk-based active carbon. *Dyes and Pigments*, 56, 219- 229.
- 39.Gray, M. N., Rock, C. A. and Pepin, R. G. 1988. Pretreating landfill leachate with biomass boiler ash. *Journal of Environmental Engineering* 114:465-470.
- 40.Gupta, G. S., Prasad, G. and Singh, V. N. 1990. Removal of chrome dye from aqueous solutions by mixed adsorbents: Fly ash and coal. *Water Research* 24:45-50.
- 41.Gupta, V. K. and Ali, I. 2001. Removal of DDD and DDE from wastewater using bagasse fly ash: A sugar industry waste. *Water Research* 35:33-40.
- 42.Gupta, V. K. and Ali, I. 2004. Removal of lead and chromium from wastewater using bagasse fly ash: A sugar industry waste. *Journal of Colloid and Interface Science* 271:321-328.
- 43.Gupta, V. K., Mittal, A. Gajbe, V. 2005. Adsorption and desorption studies of a water soluble dye, Quinoline Tellow, using waste materials. *Journal of Colloid and Interface Science* 284:89- 98.
- 44.Gupta, V.K., Mittal, A., Krishnan, L. and Gajbe, V. 2004. Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash. *Separation and Purification Technology* 40:87-96.
- 45.Haimour, N. and Sayed, S. 1997. The adsorption kinetics

of methylene blue dye on jift. *Engineering and Science* 24:215-224.46.Hamada, M. and Kumagai, H. 1988. Chemical composition of sardine scale. *Nippon Suisan Gakkaishi*. 54:1987-1992.47.Hall, K.R., Eagleton, L. C., Acrivos, A. and Vermeulen, T. 1966. Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. *Industrial and engineering chemistry fundamentals*, 5, 212-223.48.Helferrich, F. 1962. Ion-exchange. McGraw Hill, New York, U. S. A.49.Hequet, V., Ricou, P., Lecuyer, I. and Cloirec, P. L. 2001. Removal of Cu²⁺ and Zn²⁺ in aqueous solutions by sorption onto mixed fly ash. *Fuel* 80:851-856.50.Ho, Y. S. and McKay, G. 1998. Sorption of dye from aqueous solution by peat. *Chemical Engineering Journal* 70:115- 124.51.Ho, Y. S. and McKay, G. 1999. Pseudo-second order model for sorption processes. *Process Biochemistry* 34:451- 465.52.Ikoma, T., Kobayashi, H., Tanaka, J., Walsh, D., and Mann, S. 2003. Physical properties of type I collagen extracted from .sh scales of *Pagrus major* and *Oreochromis niloticas*. *International Journal of Biological Macromolecules* 32: 199 – 204.53.Jano, P., Buchtova, H. and Ryznarova, M. 2003. Sorption of dyes from aqueous solutions onto fly ash. *Water Research* 37:4938-4944.54.Karthikeyan, K. G., Elliott, H. A. and Chorover, J. 1999. Role of surface precipitation in copper sorption by the hydrous oxides of iron and aluminum. *Journal of Colloid and Interface Science* 209:72-79.55.Kima, T. H., Park, C., Yang, J. and Kima, S. 2004. Comparison of disperse and reactive dye removals by chemical coagulation and Fenton oxidation. *Journal of Hazardous Materials B* 112:95-103.56.Lagergren, S. 1989. About the theory of so called adsorption of soluble substances. *Ksver Vetenskapsakad Handl* 24:1-6.57.Li, F., Wang, Y., Wang, D. and Wei, F. 2004. Characterization of single-wall carbon nanotubes by N₂ adsorption. *Carbon* 43:2375-2383.58.Lin, C. J. and Chang, J. E. 2001. Effect of fly ash characteristics on the removal of Cu (II) from aqueous solution. *Chemosphere* 44:1185-1192.59.Lowell, S. and Shields, J. E. 1984. *Power surface area and porosity* 2nd ed. Chapman and Hall Ltd, New York, U.S.A.60.Malik, P. K. 2003. Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of acid yellow 36. *Dyes Pigments* 56:239-249.61.Malik, P. K. and Saha, S. K. 2003. Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst. *Separation and Purification Technology* 31:241-250.62.Mall, I. D., Srivastava, V. C. and Agarwal, N. K. 2006. Removal of Orange-G and Methyl Violet dyes by adsorption onto bagasse fly ash-kinetic study and equilibrium isotherm analyses. *Dyes and Pigments* 69:210-223.63.McKay, G., Blair, H. S. and Gardner, J. R. 1982. Adsorption of dyes on chitin. I: Equilibrium studies. *Journal of Applied Polymer Science* 27:3043-3057.64.McKay, G. 1984. Two-resistance mass transfer models for the adsorption of dyestuffs from solutions using activated carbon. *Journal of Chemical Technology and Biotechnology* 34A:294- 310.65.McKay, G., El-Geundi, M. and Nassar, M. M. 1987. Equilibrium studies during the removal of dye stuffs from aqueous solutions using bagasse pith. *Water Research* 21:1513-1520.66.McKay, G., Porter, J. F. and Prasad, G. R. 1999. The Removal of dye colours from Aaqueous solutions by adsorption on low-cost materials. *Air and Soil Pollution* 114:423-438.67.Meehan, C., Banat, I. M., McMullan, G., Nigam, P., Smyth, F. and Marchant, R. 2000. Decolorization of remazol Black-B using a thermotolerant yeast, *Kluyveromyces marxianus* IMB3. *Environmental International* 26:75-79.68.Morais, L. C., Freitas, O. M., Goncalves, E. P., Vasconcelos, L. T. and Gonzalez, B. C. G. 1999. Reactive dyes removal from wastewaters by adsorption on eucalyptus bark: variables that define the process. *Water Research* 33:979-988.69.Namasivayam, C., Radhika, R. and Suba, S. 2001a. Uptake of dyes by a promising locally available agricultural solid waste: coir pith. *Waste Management* 21:381-387.70.Namasivayam, C. and Kanchana, N. 1992. Waste banana pith as adsorbent for colour removal from wastewaters. *Chemosphere* 25:1691-1705.71.Namasivayam, C., Dinesh, K. M, Selvi, K., Ashruffunissa, B. R., Vanathi, T. and Yamuna, R. T. 2001b. Waste coir pith: A potential biomass for the treatment of dyeing wastewaters. *Biomass and Bioenergy* 21:477-483.72.Namasivayam, C. and Kavita, D. 2002. Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. *Dyes and Pigments* 54:47- 58.73.Namasivayam, C., Muniasamy, N., Gayatri, K., Rani, M. and Ranganathan, K. 1996. Removal of dyes from aqueous solution by cellulosic waste orange peel. *Bioresource Technology* 57:37- 43.74.Nassar, M. M., Hamoda, M. F. and Radwan, G.. H. 1995. Adsorption equilibria of basic dyestuff onto palm fruit particles. *Water Science and Technology* 32:31-41.75.Nollet, H. Roels, M. Lutgen, P. Meeren, P. Verstraete, W. 2003. Removal of PCBs from wastewater using fly ash. *Chemosphere* 53:655- 665.76.Ozcan, A., Oncu, E. M. and Ozcan, A. S. 2006. Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 277:90-97.77.Ozcan, A.S. Erdem, B. Ozcan, A. 2004. Adsorption of Acid Blue 193 from aqueous solutions onto Na – bentonite and DTMA – bentonite. *J. Colloid Interface Science* 280:44- 54.78.Onozato, H., and Watabe, N. J. 1979 *Cell Tissue Res* 201:409 – 422.79.Paszczynski, A., Pasti-grigsby, M. B., Goszczynski, S., Crawford, R. L. and Crawford, D. L. 1992. Mineralization of sulfonated azo dyes and sulfanilic acid by *Phanerochaete chrysosporium* and *Streptomyces chromofuscus*. *Applied and Environmental Microbiology* 58:3598-3604.80.Phillips, D. 1996. Environmentally friendly, productive and reliable: Priorities for cotton dyes and dyeing processes. *Journal of the Society of Dyers and Colourists* 112:183-186.81.Poots, V. J. P., Mckay, G. and Healy, J. J. 1976. The removal of acid dye from effluent using natural adsorbents I-peat. *Water Research* 10:1061-1066.82.Pagga, U. and Taeger, K. 1994. Development of a method for adsorption of dyestuffs on actived sludge. *Water Research* 28:1051-1057.83.Ricou, P., Lecuyer, I. and Cloirec, P. L. 1999. Removal of Cu²⁺, Zn²⁺ and Pb²⁺ by adsorption onto fly ash and fly ash/lime mixing. *Water Science and Technology* 39:239-247.84.Rieman, W. and Walton, H. 1970. Ion-exchange in analytical chemistry international series of monographs in analytical Chemistry. Pergamon Press, Oxford, England.85.Robinson, T., Chandran, B. and Nigan, P. 2002a. Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw. *Water Research* 36:2824- 2830.86.Robinson, T., Chandran, B. and Nigam, P. 2002b. Effect of pretreatments of three waste residues, wheat straw, corncobs and barley husks on dye adsorption. *Bioresource Technology* 85:119-124.87.Ryu, Z., Zheng, J., Wang, M. and Zhang, B. 1999. Characterization of pore size distributions on carbonaceous adsorbents by DFT. *Carbon* 37:1257-1264.88.Schneider, P. 1995. Adsorption isotherm of microporous-mesoporous solids revisited. *Applied Catalysis A:General* 129:157-165.89.Sen, A. K. and De, A. K. 1987. Adsorption of mercury (II) by coal ash. *Water research* 21:885-888.90.Slejko, F. L. 1985.

Adsorption Technology: A step-by-step approach to process evaluation and application. Dekker, New York, U. S. A.91.Slokar, Y. M., Marechal, A. and Majcen, L. 1998. Methods of decolorization of textile wastewater. *Dyes and Pigments* 37:335-356.92.Stavropoulos, G. G. 2005. Precursor materials suitability for super activated carbons production. *Fuel Processing Technology* 86:1165-1173.93.Tahir, S. S. and Rauf, N. 2006. Removal of a cationic dye from aqueous solutions by adsorption onto bentonite clay. *Chemosphere* 63:1842-1848.94.Temkin, V. I. and Pyzhev, V. 1940. Kinetics of ammonia synthesis on promoted iron catalysts. *Acta Physicochimica URSS* 12:327-356.95.Tsai, W. T., Chang, C. Y., Lin, M. C., Chien, S. F., Sun, H. F. and Hsieh, M. F. 2001. Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasses by ZnCl₂ activation. *Chemosphere* 45:51-58.96.Tseng, R. L., Wu, F. C. and Juang, R. S. 2003. Liquid-phase adsorption of dyes and phenols using pinewood-based activated carbons. *Carbon* 41:487- 495.97.Vendevivere, P. C., Bianchi, R. and Verstraete, W. 1998. Treatment and reuse of wastewater from wet-processing industry: Reviews of emerging technology. *Journal of Chemical Technology and Biotechnology* 72:289-302.98.Viraraghavan, T. and Alfaro, F. D. 1998. Adsorption of phenol from wastewater by peat, fly ash and bentonite. *Journal of Hazardous Materials* 57:59-70.99.Vlyssides, A. G., Papaioannou, D., Loizidou, M., Karlis, P. K. and Zorpas, A. A. 2004. Testing an electrochemical method for treatment of textile dye wastewater. *Waste Management* 20:569-574.100.Wang, Y. 2000. Solar photocatalytic degradation of eight commercial dyes in TiO₂ suspension. *Water Research* 34:990-994.101.Wang, C., Yediler, A., Lienert, D., Wang, Z. and Kettrup, A. 2003. Ozonation of an azo dye C.I. Remazol Black 5 and toxicological assessment of its oxidation products. *Chemosphere* 52:1225-1232.102.Wang, S. and Li, H. 2005. Dye adsorption on unburned carbon: Kinetics and equilibrium. *Journal of Hazardous Materials* B126:71- 77.103.Wong, P. K. and Yuen, P. Y. 1996. Decolorization and biodegradation of methyl red by *Klebsiella Pneumoniae* RS-13. *Water Research* 30:1763-1774.104.Wong, Y. C., Szeto, Y. S., Cheung, W. H. and McKay, G. 2004. Adsorption of acid dyes on chitosan: Equilibrium isotherm analyses. *Process Biochemistry* 39:693-702.105.Wu, G., Kaliadima, A., Her, Y. and Matijevic, E. 1997. Adsorption of dyes on nanosize modified silic particles. *Journal of Colloid and Interface Science* 195:222- 228.106.Zylberberg, L., Bonaventure, J., Cohen-Solal, L., Hartmann, D. J., Bereiter-Hahn, J. 1992. Organization and characterization of fibrillar collagens in fish scales in situ and in vitro. *Journal of Cell Science* 103:273 – 285.