

Preparation of adsorbents from sludges for adsorption of dye solutions

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ABSTRACT

The objectives of the research are to prepare the adsorbents using waste sludge as the raw material, and to study the adsorption behaviors of the single, binary, and ternary dyestuff solutions. Four single (AR4, AR27, MG, and RB5), two binary dyestuff solutions (MG+AR27 and RB5+AR4) and one ternary dyestuff solution (AR4+RB5+MG) were investigated. As for the chemical activation techniques applied to the waste sludge, the adsorbents using $ZnCl_2 + H_2SO_4$ as the activation agent was found to exhibit the greatest adsorption capability. The results showed that the adsorption of binary dye solutions could be well described by the rate equation of pseudo-second-order reaction. The saturated adsorption amount of RB5 in the binary dye solution is 22.32 mg/g, which is smaller than that in the single dye solution. As for the adsorption isotherms, the Langmuir adsorption isotherm could successfully describe most conditions. Based on the parameters derived from the adsorption of single dye solution, the isothermal adsorption equations of binary dye solutions could be predicted. Key word : Waste sludge, Chemical activation techniques, Kinetic equation, Adsorption isotherm, Dye

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REFERENCES

參考文獻 ?O王俊傑，「KOH活化法裂解都市下水污泥生成吸附劑之研究」，碩士論文，國立中央大學，桃園，民國97年12月。 ?O林文超，「廢棄活性白土對水溶液中染料之吸附特性研究」，碩士論文，私立義守大學，高雄，民國94年1月。 ?O張心翰、林欣怡，「廢污泥研製吸附劑對於染料RR141的吸附行為研究」，專題研究報告，私立大葉大學環境工程學系，彰化，民國92年6月。 ?O張書容「利用火力發電廠燃煤底灰去除染料廢水色度之研究」，碩士論文，私立大葉大學環境工程學系，彰化，民國95年6月。 ?O黃理御、洪振?、陳正彬，「廢污泥研製吸附劑對染料Acid Red 4吸附行為之研究」，專題研究報告，私立大葉大學環境工程學系，彰化，民國93年6月。 ?O黃郁珊、陳思潔、方芊涵、徐紹展，「以廢污泥研製吸附劑對於染料溶液的吸附能力之研究」，專題研究報告，私立大葉大學環境工程學系，彰化，民國95年6月。 ?O黃秉仁，「以化學方法活化廢污泥製備吸附劑對雙成分染料之吸附特性的研究」，私立大葉大學環境工程學系，彰化，民國98年6月 ?O彭詠綺、譚仁豪、林珮茹，「廢污泥研製吸附劑對雙成份染料溶液的吸附行為研究」，專題研究報告，私立大葉大學環境工程學系，彰化，民國93年1月。 ?O蔡安東，「化學活化法製備孟宗竹活性碳製程之研究」，碩士論文國立雲林科技大學，雲林，民國96年7月。 ?O潘毅峰，「再生廢白土對染料及重金屬之競爭吸附行為研究」，碩士論文，私立義守大學，高雄，民國95年7月。 ?O 謝辰芳、吳欣樺、江政穎、陳美芳、詹又寧，「廢污泥研製吸附劑對於染料Acid Red 27的吸附行為研究」，專題研究報告，私立大葉大學環境工程學系，彰化，民國93年6月。 ?O謝國鎔，「廢矽藻土活化再生為多孔性材料」，碩士論文，臺南藥理科技大學，台南，民國92年。 ?O蕭俊弘，「以自製吸附劑吸附雙成份染料與其光催化特性之研究」，碩士論文，私立大葉大學環境工程學系，彰化，民國96年6月。 ?OAcemioglu, B., " Adsorption of Congo red from aqueous solution onto calcium-rich fly ash ", Journal of Colloid and Interface Science Vol.274,pp. 371-379, 2004 ?OAI-Degs, Y., Khraisheh, M. A. M., Allen, S. J., Ahma, M. N., Walker, G.. M., " Competitive adsorption of reactive dyes from solution: Equilibrium isotherm studies insingle and multisolute systems ", Chemical Engineering Journal , Vol.128, pp.163-167, 2007. ?OAI-Qodah, Z., " Adorption of dyes using shale oil ash ", Water research Vol.34, pp. 4295-4303, 2000 ?OAllen, S. J., Mckay, G., Porter J. F., " Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems ", Journal of Colloid and Interface Science, Vol.280, pp.322-333, 2004. ?OAmn N. K., " Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel:Adsorption equilibrium and kinetics ", Journal of Hazardous Materials Vol.165,pp.52 – 62, 2009 ?OAnnadurai G., Ruey-Shin Juang R.S., Lee D.J., " Use of cellulose-based wastes for adsorption of dyes from aqueous solutions ", Journal of Hazardous Materials, Vol. B92, pp. 263 – 274, 2002 ?OBasar ,C. A., " Applicability of the various adsorption models of three dyes adsorption onto activated carbon prepared waste apricot ", Journal of Hazardous Materials, Vol.B135, pp.232-241, 2006. ?OBatzias F.A., Sidiras D.K., " Dye adsorption by calcium chloride treated beech sawdust in batch and fixed-bed systems ", Journal of Hazardous Materials, Vol. B114, pp. 167 – 174, 2004 ?OCay, S., Uyan?k, A., Ozasik, A., " Single and binary component adsorption of copper(II) and cadmium(II) from aqueous solutions using tea-industry waste ", Separation and Purification Technology, Vol.38, pp.273-280, 2004. ?OChan, L. S., Cheung, W. H., McKay,G., " Adsorption of acid dyes by bamboo derived activated carbon ", Desalination, Vol.218, pp.304-312, 2008. ?OChiang, H. L., Lin, K. H., Chen, S.Y., Choa, C. G., Pan, S. D., " Dye adsorption on biosolid adsorbents and commercially activated carbon ", Dyes and Pigments, Vol.75, pp.52-59, 2007. ?OChiou, M. S., Chuang,G. S., " Competitive adsorption of dye metanil yellow and RB15 in acid solutions on chemically cross-linked chitosan beads ", Chemosphere, Vol.62, pp.731-740, 2006. ?OChiou, M. S., Ho, P. Y., Li, H. Y., " Adsorption behavior of dye AAVN and RB4 in Acid solutions on chemically cross-linked chitosan beads ", Chem. Engrs, Vol.34, pp.625-634, 2003. ?OChoy, K. K. H., Porter,J.F., McKay, G., " Intraparticle diffusion in single and multicomponent acid dye adsorption from wastewater onto carbon ", Chemical Engineering Journal, Vol.103, pp.133-145, 2004. ?OCrini G., " Non-conventional low-cost adsorbents for dye removal: A review ", Bioresource Technology, Vol. 97, pp. 1061-1085, 2006 ?ODias J.M., Maria C.M. Alvim-Ferraz M.C.M., Manuel F. Almeida M.F., Rivera-Utrilla J., Sanchez-Polo M., " Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review ", Journal of Environmental Management, Vol. 85, pp. 833 – 846, 2007 ?ODemir H., TopA., Balko se D., U lku S., " Dye adsorption behavior of Luffa cylindrica fibers ", Journal of Hazardous Materials Vol. 153, pp. 389 – 394, 2008 ?ODemirbas A., " Agricultural based activated carbons for the removal of dyes from aqueousolutions: A review ", Journal of Hazardous Materials ,Vol. 167, pp. 1 – 9, 2009 ?ODin, A. T. M., Hameed, B. H., Ahmad, A. L., " Batch adsorption of phenol onto physiochemical-activated coconut shell ", Journal of Hazardous Materials, Vol.161, pp.1522-1529, 2009. ?OGarg V.K., Amita M., Kumar R., Gupta R., " Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste ", Dyes and Pigments, Vol. 63, pp. 243-250, 2004 ?OGupta V.K., Suhas, " Application of low-cost adsorbents for dye removal – A review ", Journal of Environmental Management, Vol. 90, pp. 2313 – 2342, 2009 ?OIp, A. W. M., Barford, J. P., McKay, G., " Production and comparison of high surface area bamboo derived active carbons ", Bioresource Technology, Vol.99, pp.8909-8916, 2008. ?OIsmadji, S., Sudaryanto, Y., Hartono, S. B., Setiawan, L. E. K., Ayucitra, A., " Activated carbon from char obtained from vacuum pyrolysis of teak sawdust: pore structure development and characterization ", Bioresource Technology ,Vol.96, pp.1364-1369, 2005. ?OKhaled A., Nemr A.E., El-Sikaily A., Abdelwahab O., " Removal of Direct N Blue-106 from artificial textile dye

effluent using activated carbon from orange peel: Adsorption isotherm and kinetic studies " , Journal of Hazardous Materials Vol. 165, pp. 100 – 110, 2009 ?OKumar P.S., Ramalingam S., Senthamarai C., Niranjanaa M., Vijayalakshmi P., Sivanesan S., " Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions " Desalination, Vol. 261, pp. 52 – 60, 2010 ?OLeechart P., Nakbanpote W., Thiravetyan P., " Application of ' waste ' wood-shaving bottom ash for adsorption of azo reactive dye " , Journal of Environmental Management , Vol. 90, pp.912 – 920, 2009 ?OLi, F., Wang, Y., Wang, D. and Wei, F., " Characterization of single-wall carbon nanotubes by N2 adsorption " , Carbon Vol.43, pp. 2375-2383, 2004 ?OLillo-Ro denas M.A., Marco-Lozar J.P., Cazorla-Amoro s D., Linares-Solano A., " Activated carbons prepared by pyrolysis of mixtures of carbon precursor/alkaline hydroxide " , J. Anal. Appl. Pyrolysis Vol.80, pp. 166-174,2007 ?OMalik, P. K., " Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics " , Journal of Hazardous Materials, Vol.113, pp.81-83, 2004. ?OMachida, M., Aikawa, M., Tatsumoto, H., " Prediction of simultaneous adsorption of Cu(II) and Pb(II) onto activated carbon by conventional Langmuir type equations " , Journal of Hazardous Materials,Vol.120, pp.271-275, 2005. ?OMittal A., Mittal J., Kurup L., " Adsorption isotherms, kinetics and column operations for the removal of hazardous dye, Tartrazine from aqueous solutions using waste materials—Bottom Ash and De-Oiled Soya, as adsorbents " Journal of Hazardous Materials, Vol.B136 pp. 567 – 578, 2006 ?OMui E.L.K., Cheung W.H., Valix M., Gordon McKay G., " Dye adsorption onto char from bamboo " , Journal of Hazardous Materials Vol.177 pp. 1001 – 1005, 2005 ?ONamane, A., Mekarzia, A., Benrachedi, K., Belhaneche-Bensemra, N., Hellal A., " Determination of adsorption capacity of activated carbon made from coffee grounds by chemical activation with ZnCl2 and H3PO4 " , Journal of Hazardous Materials, Vol.B119, pp.189-194, 2005. ?ONowicki, P., Pietrzak, R., Wachowska, H., " Siberian anthracite as a precursor material for microporous activated carbons " , Fuel, Vol.87, pp.2037-2040, 2008. ?ONuithitkul K., Srikhun S., Hirunpraditkoon S., " Kinetics and equilibrium adsorption of Basic Green 4 dye on activated carbon derived from durian peel: Effects of pyrolysis and post-treatment conditions " Journal of the Taiwan Institute of Chemical Engineers, 2010 ?O anal Y., " Kinetics of adsorption of dyes from aqueous solution using activated carbon prepared from waste apricot " , Journal of Hazardous Materials, Vol. B137, pp. 1719 – 1728, 2006 ?OOtero M., Rozada F., Calvo L.F., Garc a A.I., Mora'n A., " Kinetic and equilibrium modelling of the methylene blue removal from solution by adsorbent materials produced from sewage sludges " Biochemical Engineering Journal, Vol.15, pp. 59 – 68, 2003 ?OPrahas, Devarly., Kartika, Y., Indraswati, N., Ismadji, S., " Activated carbon from jackfruit peel waste by H3PO4 hemical ctivation:Pore structure and surface chemistry characterization " , Chemical Engineering Journal , Vol.140, pp.32-34, 2008. ?OQin, F., Wen, B., Shan, X. Q., Xie, Y. N., Liu, T., Zhang, S. Z., Khan, U., " Mechanisms of competitive adsorption of Pb, Cu, and Cd on peat " , Environmental Pollution, Vol.144, pp.669-680, 2006. ?ORafatullah M., Sulaiman O., Hashim R., Ahmad A., " Adsorption of methylene blue on low-cost adsorbents: A review " , Journal of Hazardous Materials, Vol. 177, pp. 70 – 80, 2010 ?ORicou, P., Lecuyer, I. and Cloirec, P. L., " Removal of Cu2+, Zn2+ and Pb2+ by adsorption onto fly ash/lime mixing " , Water Science and Technology, Vol.39, pp. 239-247, 1999 ?ORio S., Catherine Faur-Brasquet C., Coq L.L., Courcoux P., Cloirec L.P., " Experimental design methodology for the preparation of carbonaceous sorbents from sewage sludge by chemical activation – application to air and water treatments " Chemosphere Vol.58, pp.423 – 437, 2005 ?ORobinson T., Chandran B., Nigam P., " Effect of pretreatments of three waste residues, wheat straw,corncobs and barley husks on dye adsorption " , Bioresource Technology, Vol.85, pp. 119 – 124, 2002 ?ORos, A., M, A., Lillo-Rodenas, M. A., Fuente, E., Montes-Moran, M.A., Martin, M. J., Linares-Solano, A " High surface area materials prepared from sewage sludge-based precursors " , Chemosphere, Vol.65, pp.132-140, 2006. ?ORozada, F., Otero, M., Parra, J. B., Moran, A., Garcia, A. I., " Producing adsorbents from sewage sludge and discarded tyres Characterization and utilization for the removal of pollutants from water " , Chemical Engineering Journal, Vol.114, pp.161-169, 2005. ?OSanthy K., Selvapathy P., " Removal of reactive dyes from wastewater by adsorption on coir pith activated carbon " , Bioresource Technology, Vol. 97, pp. 1329 – 1336, 2006 ?OSchneider, P., " Adsorption isotherm of microporous- mesoporous solids revisited " , Applied Catalysis A: General Vol.129, pp. 157-165, 1995 ?OSTavropoulos, G.G., " Precursor materials suitability for super activated carbons production " , Fuel Processing Technology Vol.86, pp. 1165-1173, 2005 ?OSun Q., Yang L., " The adsorption of basic dyes from aqueous solution on modified peat – resin particle " , Water Research Vol. 37, pp. 1535 – 1544, 2003 ?OSudaryanto, Y., Hartono, S. B., Irawaty, W., Hindarso, H., Ismadji, S., " High surface area activated carbon prepared from cassava peel by chemical activation " , Bioresource Technology, Vol.97, pp.734-739, 2006. ?OSrivastava, V. C., Mall, I. D., Mishra, I. M., " Equilibrium modelling of single and binary adsorption of cadmium and nickel onto bagasse fly ash " , Chemical Engineering Journal, Vol.117, pp.79-91, 2006. ?OTsai W.T., Chang C.Y., Lin M.C., Chien S.F., Sun H.F.,Hsieh M.F., " Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by ZnCl2 activation " , Chemosphere, Vol. 45, pp. 51-58, 2001 ?OTurabik, M., " Adsorption of basic dyes from single and binary component systems onto bentonite: Simultaneous analysis of Basic Red 46 and Basic Yellow 28 by first order derivative spectrophotometric analysis method " , Journal of Hazardous Materials, Vol.158, pp.52-64, 2008 ?OValix M., Cheung W.H., McKay G., " Preparation of activated carbon using low temperature carbonisation and physical activation of high ash raw bagasse for acid dye adsorption " , Chemosphere, Vol. 56 pp. 493 – 501, 2004 ?OVieira A.P., Santana S.A.A ., Bezerra C.W.B., Hildo A.S. Silva H.A.S., Jose A.P. Chaves J.A.P., MeloJ.C.P., Filho E.C.S., Airoldi C., " Kinetics and thermodynamics of textile dye adsorption from aqueous solutions using babassu coconut mesocarp " , Journal of Hazardous Materials, Vol. 166, pp. 1272 – 1278, 2009 ?OWang, X. W., Zhu, N., Yin, B., " Preparation of sludge-based activated carbon and its application in dye wastewater treatment " , Journal of Hazardous Materials, Vol.153, pp.22-27, 2008. ?OWang, S., Ariyanto, E., " Competitive adsorption of malachite green and Pb ions on natural zeolite " , Journal of Colloid and Interface Science, Vol.314, pp.25-31, 2007. ?OWu, F. C., Tseng, R. L., Juang, R. S., " Preparation of highly microporous carbons from fir wood by KOH activation for

adsorption of dyes and phenols from water " Separation and Purification Technology, Vol.47, pp.10-19, 2005. ?OYu, L., Zhong, Q., " Preparation of adsorbents made from sewage sludges for adsorption of organic materials from wastewater " , Journal of Hazardous Materials, Vol.137, pp.359-366, 2006.