UNIVERSITI PUTRA MALAYSIA

ADSORPTION PERFORMANCE OF SYNTHESIZED BASIC BISMUTH NITRATE AND ITS TITANIUM DIOXIDE-SILVER MODIFIED SYSTEMS FOR AZO DYE REMOVAL

ESHRAQ AHMED AHMED ABDULLAH

FS 2011 68

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By

ESHRAQ AHMED AHMED ABDULLAH

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

December 2011

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Effluents from industries contain large quantities of organic and inorganic pollutants. The high cost of activated carbon restricts its application in wastewater treatments. In addition, the low efficiency of low cost materials in removing organic contaminants from aqueous solution has resulted in a significant shift of attention towards synthesizing or developing new suitable adsorbents. Thus the present study was aimed to evaluate the potential use of basic bismuth nitrate compounds as new adsorbents for azo dye removal from aqueous solution. To achieve this aim, this study was divided into four stages. Firstly, the adsorbents were synthesized by precipitation method, calcined at 723K and characterized using different analytical techniques in order to gain further insights into the chemical environment of the adsorbents' surface. Secondly, the adsorption performance of the adsorbents was evaluated using Methyl Orange (MO) and Sunset Yellow (SY) dyes as model pollutants. Thirdly, surface modification of the calcined adsorbent by addition of TiO_2 and Ag was done in order to improve its adsorption performance. The reasons behind the adsorption enhancement were proposed. The dye adsorption mechanism

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onto the adsorbents was described using isotherm shape and the hydrophilic-hydrophobic character of the adsorbent surfaces. Finally, the desorption and reusability of the adsorbents were evaluated.

TGA and XRD analyses indicated that the synthesized sample, $Bi_6O_4(OH)_4(NO_3)_6.7H_2O$ (BBN) was converted to $Bi_5O_7NO_3$ upon calcination at 723K. The addition of TiO_2 and $AgNO_3$ had resulted in the formation of TiO_2/Ag–$Bi_6O_6(OH)_2(NO_3)_4.1.5H_2O$ (PTBA0.5) which was then converted to TiO_2/Ag–$Bi_5O_7NO_3$ (TBA0.5) upon calcination. The presence of water, nitrate, hydroxyl group and octahedral TiO_2 (for TiO_2/Ag modified sample) were confirmed by FTIR and XPS spectra. TEM images and XRD analysis indicated that the TiO_2 particles were only deposited on the surface of the modified adsorbent.

The adsorption of dyes onto the adsorbents was found to be highly dependent on the adsorbent dose, initial concentration of dye and temperature. The presence of H^+ and OH^-; however, only played an important role in the adsorption process onto the calcined adsorbents. The uncalcined adsorbents demonstrated a better ability to remove methyl orange and sunset yellow dyes with shorter equilibrium time compared to that of calcined adsorbents. The high adsorption capacities of uncalcined adsorbent basic bismuth nitrate, BBN, could be attributed to its lower pH_{pzc} and surface area. The TiO_2/Ag modified adsorbent also showed higher adsorption capacities compared to the unmodified adsorbents. The enhancement in the adsorption performance could be attributed to the increase in the hydrophilic character of the adsorbent which in turn increase the electrostatic attraction with the

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anionic dye molecules. Other than that, effect of pore volume of modified adsorbents may produce a better environment for adsorption of the dye molecules.

The adsorption kinetics of azo dye onto uncalcined adsorbents obeyed the pseudo-second order reaction, indicating that the removal behaviour might be preceded via chemisorption mechanism. Although intra-particle diffusion could only be the rate limiting step of uptake behaviour at a certain stage, the film diffusion had a significant contribution on dye adsorption onto uncalcined sample. However, first-order and Langmuir 1,2–mixed order kinetics reaction gave the best description of azo dye adsorption onto calcined adsorbents.

The maximum adsorption capacities for complete monolayer coverage were 35.7, 55.6, 15.9, and 26.3 mg g^{-1} for methyl orange dye adsorption onto BBN, PTBA0.5, $Bi_5O_7NO_3$ and TBA0.5, respectively. The estimated values of sunset yellow dye removal were 25.6 and 31.3 mg g^{-1} for BBN and PTBA0.5, respectively, and 23.3 mg g^{-1} for TBA0.5, which sufficiently good compared to some synthesized adsorbents derived from low-cost materials. The adsorption efficiencies were 9.66 $\times 10^{-24}$, 26.98 $\times 10^{-24}$, 30.39 $\times 10^{-24}$ and 20.6 $\times 10^{-24}$ mmol nm^{-2} for methyl orange dye adsorption onto BBN, PTBA0.5, $Bi_5O_7NO_3$ and TBA0.5, respectively. The estimated values of sunset yellow dye removal were 5.01 $\times 10^{-24}$ and 10.99 $\times 10^{-24}$ mmol nm^{-2} for BBN and PTBA0.5, respectively, and 13.2 $\times 10^{-24}$ mmol nm^{-2} for TBA0.5. These values are more than the reported values for porous carbon suggesting the potential use of basic bismuth nitrate adsorbents in wastewater treatments. Overall, the prepared materials can be effectively used as new adsorbents for organic pollutant removal.

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Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PRESTASI ERAPAN BISMUT NITRAT BERBES YANG DISINTESIS DAN SISTEMNYA YANG DIUBAHSUAI DENGAN TITANIUM DIOKSIDA-ARGENTUM UNTUK PENYINGKIRAN PEWARNA AZO

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Efluen dari industri mengandungi kuantiti bahan pencemar organik dan bukan organik yang banyak. Kos karbon aktif yang tinggi menyekat penggunaannya dalam rawatan sisa air buangan. Di samping itu, kecekapan bahan kos rendah dalam menyingkirkan bahan cemar organik dari larutan akueus yang rendah telah menyebabkan peralihan perhatian yang signifikan ke arah penyediaan penjerap baharu yang sesuai. Oleh itu, kajian ini bertujuan untuk menilai potensi penggunaan sebatian bismut nitrat berbes sebagai penjerap baru untuk penyingkiran pewarna azo dari larutan akueus. Untuk mencapai matlamat ini, kajian ini telah dibahagikan kepada empat peringkat. Pertama, penjerap disintesis dengan kaedah pemendakan, dikalsin pada 723K dan dicirikan dengan menggunakan teknik analisis yang berbeza untuk mendapatkan beberapa maklumat terhadap persekitaran kimia permukaan penjerap ini. Kedua, prestasi jerapan penjerap dinilai dengan menggunakan pewarna Metil Jingga (MO) dan Sunset Yellow (SY) sebagai model bahan pencemar. Ketiga, pengubahsuaian permukaan penjerap yang dikalsin dengan penambahan TiO_2 dan Ag telah dilakukan untuk meningkatkan prestasi jerapan. Alasan di sebalik peningkatan penjerapan telah dicadangkan. Mekanisme penjerapan pewarna ke atas

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penjerap dijelaskan dengan menggunakan bentuk isoterma dan ciri-ciri hidrofilik-hidrofobik permukaan penjerap. Akhir sekali, penyahjerapan dan penggunaan semula penjerap turut dinilai.

Analisis TGA dan XRD menunjukkan bahawa sampel yang disintesis adalah $Bi_6O_4(OH)_4(NO_3)_6.7H_2O$ (BBN) yang bertukar kepada $Bi_5O_7NO_3$ selepas proses pengkalsinan pada 723K. Penambahan TiO_2 dan $AgNO_3$ mengakibatkan pembentukan TiO_2/Ag–$Bi_6O_6(OH)_2$ $(NO_3)_4.1.5H_2O$ (PTBA0.5) yang juga bertukar kepada TiO_2/Ag–$Bi_5O_7NO_3$ (TBA0.5) selepas proses pengkalsinan. Kehadiran air, nitrat, kumpulan hidroksil dan TiO_2 oktahedral (sampel yang diubahsuai dengan TiO_2/Ag) telah disahkan oleh spektra FTIR dan XPS. Imej TEM dan analisis XRD menunjukkan bahawa zarah TiO_2 hanya dilonggokkan di atas permukaan penjerap yang diubahsuai.

Penjerapan pewarna keatas penjerap didapati sangat bergantung kepada dos penjerap, kepekatan awal pewarna dan suhu. Kehadiran H^+ dan OH^-, akan tetapi, hanya memainkan peranan yang penting dalam proses penjerapan ke penjerap yang telah dikalsin. Penjerap yang tidak dikalsin menunjukkan keupayaan yang lebih baik untuk menyingkir pewarna metil jingga dan sunset yellow dengan masa keseimbangan yang lebih pendek berbanding dengan penjerap yang telah dikalsin. Penjerapan berkapasiti tinggi penjerap yang tidak dikalsin mungkin disebabkan oleh pH_{pzc} yang lebih rendah dan luas permukaan. Penjerap yang diubahsuai dengan TiO_2/Ag juga menunjukkan kapasiti jerapan yang lebih tinggi berbanding penjerap yang tidak diubahsuai. Peningkatan dalam prestasi penjerapan boleh dikaitkan dengan peningkatan dalam ciri-ciri hidrofilik penjerap yang seterusnya

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meningkatkan daya tarikan elektrostatik dengan molekul pewarna anionik. Di samping itu, kesan isipadu liang penjerap diubahsuai boleh menghasilkan persekitaran yang lebih baik untuk penjerapan molekul pewarna.

Kinetik penjerapan pewarna azo ke atas penjerap yang tidak dikalsin adalah mengikut tindak balas tertib pseudo-kedua yang menunjukkan bahawa tingkah laku penyingkiran mungkin melalui mekanisme erapan kimia. Walau bagaimanapun, tindak balas tertib pertama dan tertib campuran 1,2–Langmuir dapat memberi keterangan terbaik berkaitan erapan pewarna azo ke penjerap yang dikalsin. Walaupun, resapan antara zarah boleh menjadi langkah penghad kadar bagi tingkah laku penjerapan pada peringkat tertentu, peresapan filem memberi sumbangan yang besar ke atas erapan pewarna oleh sampel yang tidak dikalsin.

Kapasiti penjerapan maksimum untuk liputan ekalapisan bagi penjerapan metil jingga ke atas BBN, PTBA0.5, $Bi_5O_7NO_3$ dan TBA0.5 masing-masing adalah 35.7, 55.6, 15.9, dan 26.3 mg g^{-1}. Anggaran nilai penying sunset yellow adalah 25.6 dan 31.3 mg g^{-1} masing-masing untuk BBN dan PTBA0.5 dan 23.3 mg g^{-1} bagi TBA0.5, adalah lebih baik berbanding dengan beberapa adsorben yang disintesis daripada bahan berkos rendah. Kecekapan penjerapan bagi penjerapan metil jingga oleh ke atas BBN, PTBA0.5, $Bi_5O_7NO_3$ dan TBA0.5 masing-masing adalah 9.66×10^{-24}, 26.98×10^{-24}, 30.39×10^{-24} and 20.6×10^{-24} mmol nm^{-2}. Anggaran nilai penying sunset yellow adalah 5.01×10^{-24} dan 10.99×10^{-24} mmol nm^{-2} masing-masing untuk BBN dan PTBA0.5 dan 13.2×10^{-24} bagi TBA0.5. Nilai ini adalah lebih tinggi daripada nilai yang dilaporkan bagi karbon yang poros menunjukkan potensi adsorben bismut nitrat berbes dalam rawatan sisa air. Secara keseluruhannya,

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bahan-bahan yang disediakan boleh digunakan dengan berkesan sebagai penjerap baharu untuk penyingkiran bahan pencemar organik.

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ACKNOWLEDGEMENTS

It is a pleasure to thank the people who have contributed immensely towards this thesis. First of all, to Dr. Abdul Halim Abdullah, he is indeed a great brother and teacher, and I want to give him my deepest respect and thanks as he accepted me as his student and gave me thoughtful advice and encouragement. Prof. Dr. Zulkarnain Zainal, Prof. Dr. Mohd Zobir Hussein and Dr. Tan Kar Ban for their kind support, guidance and suggestions. Secondly, I want to say thank you for all UPM staff, faculty of sicenc, chemistry department, special grateful go to Mr. Nordin, Mr. Isharuddin and Mr. Zainal, who allowed me to run my experiments, without them I colud not have written this thesis. Also I would like to show my gratitude to Mr. Hanif, Yadoallah, Lee and all my labmates for their helps friendship. Last but not least, I would like to thank all my family members. My heartfult appaciation also to dedicated my parents for providing me with the opportunity to where I am, without them I could not be able to accomplish any thing. My great thanks should send to Yemen, Malaysia and UPM that facilitate all the difficulties that stand in front of my study.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of **Doctor of Philosophy of Science**. The members of the Supervisory Committee were as follows:

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

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ESHRAQ AHMED AHMED ABDULLAH

Date: 21 December 2011

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