REMOVAL OF DYES BY SILICA NANOPARTICLES WITH IMMOBILIZED LACCASE

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To my beloved parent and family

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ABSTRACT

Dyes give a big impact on ecosystem; thus several methods have been developed for dye removal processes. This study investigated the dye removal by the combination of adsorption and biodegradation process. Silica nanoparticles (SN), modified silica nanoparticle (MSN), silica nanoparticle with laccase (SNL), and modified silica nanoparticle with laccase (MSNL) were synthesized. All samples were characterized with scanning electron microscope (SEM), nitrogen adsorption-desorption (NAD), Fourier transform infrared (FTIR), and energy dispersive X-ray (EDX). It was found that the introduction of cationic surfactant and laccase did not change the morphology but it affected the surface area, pore characteristics and chemical properties of the SN. The dye adsorption performance using SN and MSN was evaluated in batch adsorption experiment at various experimental conditions. The adsorption of methylene blue (MB) by SN showed a good adsorption performance (q_e = 0.2291 mmol/g) as compared to the MSN (q_e = 0.0430 mmol/g). In contrast, for methyl orange (MO), the MSN showed a very good adsorption performance (q_e = 0.1849 mmol/g), while no adsorption was observed for the SN. The pH values did not give any significant effect on the dye adsorption and the cetyltrimethylammonium bromide (CTAB) concentration of 1mM was found to be the maximum value for SN modification. The adsorption equilibrium and kinetic data for both MO and MB fit the Temkin and Langmuir isotherm models well, respectively while the kinetic adsorption data follows the Elovich kinetic model with film diffusion found to be the rate-limiting step. The dye adsorption process was found to be exothermic, spontaneous and physisorption. The regeneration shows that SN and MSN are reusable for multiple cycles. For the laccase immobilization, MSN performed higher laccase adsorption (1.6696 μmol/g) as compared to SN (1.1047 μmol/g). The removal of dye by SNL and MSNL was analyzed in term of adsorption and degradation of both MO and MB dyes. Results show that the removal of MB by SNL was higher (q_e = 0.2573 mmol/g) than SN (q_e = 0.2291 mmol/g). Meanwhile, removal of MO by MSNL was higher (q_e = 0.2454 mmol/g) as compared to MSN (q_e = 0.1849 mmol/g). These results demonstrated that the surface modification of SN by cationic surfactant gave higher catalytic activity of laccase, hence giving higher removal performance of dye. The adsorption isotherm data analysis shows that the SNL and MSNL are well fitted to the Langmuir and Temkin model respectively. The Elovich kinetic model is however the best model to describe the dye adsorption kinetic data of both SNL and MSNL. The dye removal by degradation was analyzed using Michaelis-Menten enzymatic reaction equation which found that higher specific activity was observed for MSNL (88.5724 U/g) as compared to SNL (22.6360 U/g). This resulted in higher initial enzymatic reaction velocity, V_{max} (58.0 μM/min) for MO (MSNL) and lower for MB (SNL) (58.0 μM/min).

ABSTRAK

Pencelup memberi kesan buruk kepada ekosistem; jadi beberapa cara penyingkiran dikaji. Kajian ini mengkaji penyingkiran pencelup dengan gabungan proses penjerapan dan penguraian. Silika berzarah nano (SN), silika berzarah nano terubahsuai (MSN), silika berzarah nano dengan lakase (SNL), dan silika berzarah nano terubahsuai dengan lakase (MSNL) telah disintesis. Semua sampel dicirikan dengan mikroskop elektron imbasan (SEM), penganalisis penjerapan-penyahjerapan nitrogen (NAD), spektrometer Fourier transformasi infrared (FTIR) dan pembelau serakan tenaga sinar-X (EDX). Didapati kation surfaktan tidak mengubah morfologi tetapi menjejaskan luas permukaan, ciri liang dan sifat kimia SN. Penjerapan pencelup menggunakan SN dan MSN dinilai dalam eksperimen berkumpulan pada beberapa keadaan. Penjerapan pencelup biru (MB) oleh SN menunjukkan penjerapan yang baik (q_e = 0.2291 mmol/g) berbanding dengan MSN. Sebaliknya, untuk pencelup jingga (MO), MSN menunjukkan penjerapan yang sangat baik (q_e = 0.1849 mmol/g), manakala tiada penjerapan pada SN. Nilai pH tidak memberi kesan yang ketara terhadap penjerapan dan kepekatan *cetyltrimethylammonium bromide* (CTAB) 1 mM didapati adalah nilai maksimum bagi pengubahsuaian SN. Data penjerapan keseimbangan untuk kedua-dua pencelup MO dan MB berkation masing-masing mematuhi model sesuhu *Temkin* dan *Langmuir*, manakala data penjerapan kinetik mematuhi model kinetik *Elovich* dengan resapan filem sebagai kadar yang mengehadkan. Proses penjerapan adalah tindak balas luah haba, spontan dan jerapan fizikal. Penjanaan semula SN dan MSN adalah berjaya untuk beberapa kitaran. Untuk pengubahsuian lakase, MSN menunjukkan penjerapan lakase yang tinggi (1,6696 μmol/g) berbanding SN (1,1047 μmol/g). Penyingkiran pencelup oleh SNL dan MSNL telah dianalisis dari segi penjerapan dan penguraian untuk kedua-dua pencelup MO dan MB. Keputusan menunjukkan bahawa penyingkiran MB oleh SNL adalah tinggi (q_e = 0.2573 mmol/g) daripada SN (q_e = 0.2291 mmol/g). Manakala, penyingkiran MO oleh MSNL adalah tinggi (q_e = 0.2454 mmol/g) berbanding MSN (q_e = 0.1849 mmol/g). Ini menunjukkan pengubahsuaian permukaan SN oleh bahan permukaan berkation meningkatkan aktiviti pemangkinan lakase dan seterusnya memberikan penyingkiran pencelup yang tinggi. Data penjerapan, garis sesuhu menunjukkan bahawa SNL dan MSNL masing-masing mematuhi dengan baik model sesuhu *Langmuir* dan *Temkin*. Model kinetik *Elovich* adalah model yang sesuai bagi penjerapan pencelup oleh SNL dan MSNL. Penyingkiran pencelup secara penguraian pula dinilai menggunakan persamaan tindakbalas enzim *Michaelis-Menten* yang mendapati bahawa aktiviti pemangkin adalah lebih tinggi pada MSNL (88.5724 U/g) jika dibandingkan dengan SNL (22.6360 U/g). Ini membawa kepada kelajuan tindak balas awal enzim, Vmax (58.0 μM / min) yang tinggi untuk MO (MSNL) dan rendah untuk MB (SNL) (58.0 μM/min).