Dimethoxytriazine-Triazole Linked Mesoporous Silica Hybrid Sorbent for Cationic Dyes Adsorption

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Graphical abstract

Abstract

Organic dye has always been considered one of the most serious water pollutants. Therefore, the great significance nowadays is to synthesis effective adsorbent Materials for removal of these contaminants. Herein, we prepared successfully a novel sorbent based on dimethoxytriazine/triazole groups functionalized via a 1,3-dipolar cycloaddition click reaction on mesoporous silica SBA-15. The resulting sample denoted DMT-Tr-SBA-15 was characterized by FTIR spectra, X-ray photoelectron spectroscopy (XPS), solid-state ^{13}C NMR spectroscopy and nitrogen adsorption/desorption isotherm. The resulting hybrid silica material was evaluated as a sorbent for adsorption of four cationic dyes in aqueous media showed high adsorption efficiency and a fast removal rate. The adsorption properties were monitored versus time; the after 40 min and using a 40 mg/L of adsorbent was reached. The maximum adsorption capacity for methylene blue at room temperature and neutral pH was 4.59 mmol g^{-1} . These results indicate the great potential of clickable mesoporous silica to diversify the active sites for adsorption, thus demonstrating a significant interest for environmental applications.

Keywords: mesoporous SBA-15, triazine/triazole, 1,3-dipolar cycloaddition, adsorption, dye removal.

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1. Introduction

Organic dye pollutants have been extensively used for a long time in various industrial fields such as printing, textile, and cosmetics [1]. Some of these dyes can cause various diseases and carcinogenic effects in humans and negative impacts on the environment [2]. To address this concern, many processes have been developed for dyes removal such as photocatalysis [3, 4], membrane filtration [5], ultrafiltration [6] and adsorption [7,8,9]. Among them, adsorption has emerged as potential, low cost, simple and efficient alternative [10]. Therefore, the synthesis of new convenient adsorbent with high adsorption capacity is extremely significant.

Ordered mesoporous silica (OMS) have large surface area and accessible pore volume [11,12] which make them suitable materials for the efficient adsorption of a wide range of pollutants [13]. However, the mesoporous silica with its surface containing inert silanol groups cannot be used directly without modification [14]. Therefore, organic ligands can be immobilized on mesoporous silica via functionalization of those silanol groups $\equiv\text{Si-OH}$. To date, several functional groups containing donor atoms (i.e., O/N/S/P) were successfully decorated OMS and used for organic pollutants adsorption and heavy metal extraction, namely : Bis (2 benzimidazolyl)pyridine (bbp) [15], thenoyltrifluoroacetone (TTA) [16], benzene-1,3,5-triamido-tetraphosphonic acid [17], carboxylic acid [18] and phosphoryl functionalized OMS [19].

Among the wide variety of possible reactions for functionalization, Copper (I) catalyzed azide–alkyne cycloaddition (CuAAC) click reaction is a common approach to introduce electron-rich heterocycles on mesoporous silica [20,21,22] which received remarkable interest in various fields such as removal of antibiotics [23], catalyst supports [24,25], immobilization of enzymes [26] and biosensing applications [27]. Recently, a huge number of significant researchers on triazol modified mesoporous silica have been reported in literature as adsorbents (**Table 1**).

Table 1: Recent triazol linked mesoporous silica via azide–alkyne cycloaddition to generate hybrid adsorbents.

N₃-Mesoporous silica	Grafted molecules	Sorbates	ref
N ₃ -SBA-15	phenylacetylene	Phenols	[28]
N ₃ -SBA-15	propargylamine propargylsulfone	Niobium and copper species	[29]
N ₃ -HNS (Hollow nanostructured silica)	1-heptyne 2-butyne-1,4-diol propargyl alcohol phenylacetylene	Antibiotics	[23]
N ₃ - Silica	10-undecynoic acid	Neutral and acidic drugs	[30]
N ₃ - SBA-15	3-ethynyl-1-methylimidazole	5-amino-4-hydroxy-7-sulfonaphthalene-2-sulfonate anion (H-acid)	[31]
N ₃ - SBA-15	propargyl alcohol	Copper	[32]

Electron-rich heterocycles allow the hybrid material to interact easily with organic dyes by variety of possible adsorption mechanisms such as π – π hydrophobic, electrostatic interaction, Vander Waals forces, hydrogen bonding or coordinative bond that makes them suitable for the adsorption and/or catalytic application [33, 34]. For instance, in our previous work we constructed triazole/triazine-functionalized SBA-15 through CuAAC and subsequently we immobilized the palladium nanoparticles used efficiently for the catalytic reduction of 4-nitrophenol [25]. In this context, Taheri and coworkers reported dendrimer amines based on 1,3,5-triazines modified MCM-48 as efficient silver ions removal from aqueous solution and electroplating industry wastewater [35].

Taking advantage of the outstanding properties of OMS and electron-rich heterocycles, herein, we selected N-rich linker dimethoxy 1,3,5-triazine complexes as ligands to synthesize a novel hybrid material denoted DMT-Tr-SBA-15. The schematic process to produce the ligand-modified mesoporous silica is displayed in **Figure 1**. We firstly start by modification of the SBA-15 by an azido-propylsilane. Then in second step the propargyl-4,6-dimethoxy-1,3,5-triazine N-rich ligand was synthesized from 2-Chloro-4,6-dimethoxy-1,3,5-triazine by reaction with propargylamine. As a third step, we used the conventional click coupling

reaction between azido groups attached to SBA-15 (N₃-SBA-15) and the alkyne group from modified triazine ligand in the presence of copper species as catalyst. Finally, the hybrid material DMT-Tr-SBA-15 was evaluated as adsorbent for removal of four cationic dyes from an aqueous media. The hybrid material showed high adsorption efficiency and fast removal rate. The maximum adsorption capacity for methylene blue at room temperature and natural pH was 4.59 mmol g⁻¹ within 40 min for a 40 mg/L.

Figure .1. Molecular view of dimethoxytriazine/triazole linked covalent mesoporous silica preparation.

2. Experimental section

2.1. Material

Poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethyleneoxide) [EO₂₀PO₇₀EO₂₀, Pluronic P123, Mw =5800], tetraethylorthosilicate (TEOS, 98%), propargylamine, 3 chloropropyltriethoxysilane, 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT), , acetone, triethylamine, tetrahexylammonium bromide, sodium azide (NaN₃), acetonitrile (ACN), anhydrous pentane, anhydrous toluene, copper sulfate (CuSO₄), sodium ascorbate,

dimethylformamide (DMF), HCl, ethanol, and propan-2-ol. Water was deionized using the Milli-Q system of Millipore.

2.2. Synthesis of SBA-15 mesoporous silica

SBA-15 mesoporous silica was prepared along the method previously described by Zhao *et al.* [36]. Briefly, Pluronic P123 was mixed with HCl (3g /16.5 ml); the mixture was diluted using 112 ml of deionized water and stirred for three hours at 40 °C, then TEOS (7.427 g) was added to the mixture. After 2h (at 40 °C) a gel was formed, and the mixture was transferred for condensation at 90 °C for 24 h. Following drying and washing, the organic template was removed by calcination at (550 °C with a heating rate set at 2°C min⁻¹, under air and at set final temperature the solid was left 6h).

2.3. Preparation of dimethoxytriazine/triazole linked covalent mesoporous SBA-15

2.3.1. Synthesis of the azidopropyltriethoxysilane-functionalized SBA-15

The used 3-azidopropyltriethoxysilane coupling agent (AZPTES) was fabricated as described in [37]. The as prepared silane (AZPTES) was colorless liquid. ¹H NMR (CDCl₃): δ (ppm) = 3.75 (q, 6 H; CH₃CH₂O), 3.20 (t, 2H; CH₂N₃), 1.64 (m, 2H; SiCH₂CH₂), 1.16 (t, 9H, CH₃CH₂O), 0.61 (m, 2H; SiCH₂) (see Figure S1). The functionalization was done by dissolving of 1g of SBA-1 in 50 mL of toluene, then 2 mL AZPTES were added under nitrogen atmosphere, and the mixture was stirred for 24 h at 80 °C. After the completion of reaction, the mixture was cooled, filtered and washed with toluene and ethanol.

2.3.2 Synthesis of 2-Propargyl-4, 6-dimethoxy-1, 3, 5-triazine (PDMT)

Firstly, (1.2 g, 6.9 mmol) of 2-Chloro-4,6-dimethoxy-1,3,5-triazine was added to a mixture of propargylamine (0.45 g, 8.2 mmol) and triethylamine (0.57 g, 6.9 mmol) in 120 mL acetone. The solution was then heated, filtered, then dried under vacuum¹. The final isolated product is a white powder. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 5.7 (H, N-H); δ (ppm) = 4.15 (dd, 2H, N-CH₂-C); δ (ppm) = 3.9 (d, 6H, O-CH₃); 2.2(t, H, alkyne C-H) (see Figure S2).

2.3.3 Preparation of DMT-Tr-SBA-15.

4, 6-dimethoxy 1,2,3-Triazole -1,3,5-Triazine (DMT-Tr) ligand decorated SBA-15 was obtained by 1,3-dipolar cycloaddition reactions. First, 1.22 g of N₃-SBA-15, 0.43g of CuSO₄ (0.1M), and 0.77 g of sodium ascorbate solution (0.1M) was added to a solution of 2-propargy-4,6-dimethoxy-1,3,5-triazine (0.47g, 1M) in 50% aqueous propan-2-ol (20 ml). The obtained mixture was mixed for 24 h at room temperature. After filtration, washing and vacuum drying, the final product was isolated and abbreviated DMT-Tr-SBA-15.

2.4. Adsorption experiments

Adsorption experiments was carried out at room temperature by contacting specified amount (30 mg) of DMT-Tr-SBA-15 adsorbent with 50 mL of organic dyes in 100 mL glass bottles placed in magnetic stirrer agitated at 300 rpm for a predefined time at 25°C. After skipping equilibrium time, the mixture filtered through a membrane filter to separate the solid and liquid phases. The dyes concentrations in the filtrates were determined on a UV-Vis spectrophotometer at the maximum absorbance of each dye. The dye removal percentage was calculated by the following equation (Eq. (1)) $R \% = \left[\frac{C_0 - C_{eq}}{C_0} \right] \times 100$ Where C_0 and C_{eq} are the initial and equilibrium concentration of organic dye (mg L⁻¹), respectively. The amount of dye adsorbed (q_t) was calculated by the following equation (Eq. (2)): $q_t = \left[\frac{(C_0 - C_t) \times V}{m} \right]$ Where q_t is the amount of dye adsorbed and C_t is the dye concentration in the solution at time t and m amount of sorbent (g).

2.5. Characterization

The ¹H, and ¹³C NMR spectra were acquired, using Bruker AVANCE 300 wide bore spectrometer using deuterated chloroform as the solvent and internal standard. Fourier transform infrared (FTIR) spectra were recorded using an EQUINOX 55 (Bruker) spectrometer ranging from 4000 to 400 cm⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were made using a K Alpha (Thermo) fitted with a monochromatic Al K X-ray source (spot size: 400 μm). The spectra were calibrated against the C1s component set at 284.9 eV. Thermogravimetric analyses were performed using a SETSYS evolution 16 apparatus from SETARAM by heating up the sample from room temperature up to 800°C under air flow (55 cm³ (STP)/min) with a heating rate of 10 °C min⁻¹. Nitrogen adsorption and

desorption studies were carried using an autosorb IQ Quantachrome. The specific surface (S_{BET}) values were obtained using the Brunauer-Emmett-Teller (BET) method, [38] while the mesopore size study of the materials was carried out using the Barrett-Joyner-Halenda (BJH) method [39].

3. Results and discussion

3.1. Physicochemical properties of materials.

3.1.1. Fourier transform infrared spectroscopic analysis.

The dimethoxy-triazine ligand FT-IR changes upon modification are presented in **Figure .2a**. The spectrum of pure 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT) exhibits the characteristic absorption bands in the 478–1662 cm^{-1} range (i.e., 1562, 1460, 1300, 818 and 558 cm^{-1}) can be assigned to aromatic stretching modes in triazine ring, C-N, C=N, C-N stretchings, and C-H bending vibrations. After reaction with propargylamine, once can note that triazine ring appear. As well as, the new adsorption peaks at 2109, 2923, 2961, 3128 and 3244 cm^{-1} can be assigned to (C-C $\equiv$ CH) stretch, ν_{sy} CH in -CH₂ – group) , ν_{as} CH (in -CH₂ – group) , (N-H secondary amine) and ($\equiv$ CH) stretch respectively. All of these bands confirmed the successful synthesis and confirm ¹H NMR result. In other hand Figure .2b shows the synthesis of (3-azidopropyl) triethoxysilane from 3-chloropropyltriethoxysilane. We can clearly observe that after modification a new peak appear at 2095 cm^{-1} can be ascribed to the azido groups [23,40]. On the other hand, Figure .3b shows the spectra of SBA-15-based materials. All samples exhibited a band at 960 cm^{-1} is a characteristic peak of asymmetric stretching vibrations Si-O-S [41]. The associated Si-O-Si bands are observed at 1274, 1050, 910, 797, and 448 cm^{-1} [37]. After azido-silanization, an obvious adsorption peak at 2110 is observed which is a characteristic stretching vibration of organic azides [23]. After the click reaction, the absorbance corresponding to the azido group decreases significantly and

disappears. A new bands are observed in the spectrum of DMT-Tr-SBA-15 between 1589 and 1376 cm^{-1} can be assigned to ring stretching vibration of conjugated C=N and stretching C–N of primary, secondary amines and in triazine and triazole rings respectively, giving an evidence of the successful functionalization of the OMS pristine .

Figure.2. FT-IR spectra of: (a) dimethoxy-triazine ligand before and after modification with propargylamine, (b) synthesis of (3-azidopropyl)triethoxysilane from 3-chloropropyltriethoxysilane and (c) SBA-15-based materials before and after modification steps.

3.1.2. ^{13}C solid-state NMR analysis

To confirm FTIR studies above, we have employed the NMR Solid-state ^{13}C CP/MAS. NMR spectra of $\text{N}_3\text{-SBA-15}$ and DMT-Tr-SBA-15 are displayed in Figure.3. $\text{N}_3\text{-SBA-15}$ spectra show three peaks at $\delta = 9.4$, 22.5 and 54 ppm can be attributed to the first carbon (C1) attached to Si, the middle carbon (C2) and the third carbon (C3) attached to the azido groups, respectively [42]. It can be noticing also the appearance of tow additional peaks signals can be associated to residual P123 template (71, 17 ppm) and EtO-groups (59 and 17 ppm) the same as previous reports [43]. However, after azide-alkyne modification, extra newly peaks are clearly appeared at $\delta = 120$, 145, 165 and 170 ppm, which corresponds to the carbons present in the rings of triazole/triazine attached to the surface. The appearance of smaller peak at 37 ppm in the ^{13}C NMR spectrum of DMT-Tr-SBA-15 corresponds to carbon attached to the oxygen atom in the methoxy group of triazine heterocycles.

Figure.3. Solid-state ^{13}C CP/MAS NMR spectra of $\text{N}_3\text{-SBA-15}$ and DMT-Tr-SBA-15 . *Surfactant signals (P123).

3.1.3. X-ray Photoelectron Spectroscopic Analysis.

Meanwhile, to characterize the surface chemistry and chemical composition we employed XPS. Survey spectra of pristine and modified mesoporous silica are shown in Figure. 4. In addition to Si2p (~ 105 eV), Si2s (~ 155 eV) and O1s (~ 532 eV), SBA-15 exhibits a very low

intensity C1s peak due to adventitious hydrocarbon contamination. After chemical reaction with AzPTES the survey spectrum shows the appearance of the N1s feature centered at ~399 eV it is strong supporting evidence of the attachment of azidopropyl groups onto surface. This is accompanied by an attenuation of Si2p and Si2s peaks. After CuAAC reaction, C and N contents increase as the DMT-TrSBA-15 sample; this in agreement with the decrease of the silicon and oxygen atomic percents (Table S1, Supporting Information).

Figure. 4. XPS survey spectra for different SBA-15 materials.

C1s and N1s high resolution regions before and after azide–alkyne 1,3-dipolar cycloaddition are shown in Figure 5. The C1s high resolution XPS spectrum from N₃-SBA-15 (Figure 5a) is fitted with three components centered at 284.9, 286.7 and 288.7 eV, can be assigned to C-C/C-H, N-C and O-C=O chemical environments, respectively. The high binding energy component O-C=O could originate from SBA-15; this component is invariably detected at the surface of high energy materials such as metals, metal oxides and ceramics [44]. After click reaction, for DMT-Tr-SBA-15, the peak-fitted C1s spectrum of DMT-Tr-SBA-15 (Figure. 5c) shows three peaks at the binding energy values 288.3, 286.3, and 284.2 eV; they can be attributed to N=C/C=C, N-C/CO and C-C/C-H chemical environments, respectively. It follows a relative increase in the N=C/C=C, N-C/CO intensity as a proof of the presence of triazine and triazine rings onto surface.

The N1s of N₃-SBA-15 (Figure 5b) was fitted in three components; assigned to quaternized –C-N=N⁺=N⁻ (~404.5 eV), –N=N⁺=N⁻/N-C (~401 eV) and N-H/N-C (399–400 eV) [25]. The positively charged nitrogen from the azido group coexists in $\text{—N=N}^+=\text{N}^- \leftrightarrow \text{—N—N}^+ \equiv \text{N}$ mesomeric structures [45]. The main peak centered at ~401 is due to the two other nitrogen atoms which can be negatively charged (see mesomeric structures). After the click reaction, the azide is transformed into triazole and the N⁺ peak component, disappeared indicating the successful reaction. The surface analysis results are in line with the FTIR findings (Figure 2). The sp³ nitrogen atom has two peaks located at 401.1 eV ascribed to NH⁺ groups and/or triazole N⁺ atoms respectively. The N=N atoms have a single component centered at 399.8 eV. The first peak at 398.9 eV is assigned to N=C bonds in triazole and triazine rings.

Figure.5. Peak-fitted C1s and N1s regions from N₃-SBA-15 before cycloaddition (b, c) and after (d, e).

3.1.4. Thermal Analysis.

Further to confirm the successful modification, of OMS with the functional groups, thermal stability of all the synthesized materials was studied by thermogravimetric analysis (TGA) under N₂ atmosphere from room temperature to 800 °C under a rate of 10 °C min⁻¹. The plots of pristine are also reported which does not show any significant weight loss due to its higher thermal stability imparted by the strong Si-O-Si bonds. As shown in Figure 6 the first weight loss stage below 190°C correlated to adsorbed physical water, with a total weight loss of 2.06% and 6.95 % for N₃-SBA-15 and DMT-Tr-SBA-15, respectively. Above 250°C a massive thermal decomposition is observed for N₃-SBA-15 and DMT-Tr-SBA-15 with a total weight loss of 13.5% and 24.6%, respectively. The second weight loss is due to decomposition of the residual surfactant for the pristine and decomposition of the functional groups decorated the OMS network. It is important to note that the weight loss difference between N₃-SBA-15 and DMT-Tr-SBA-15 is about 11.1% which is an indication of substantial anchoring of triazole/triazine rings to the mesoporous silica surface.

Figure. 6. Thermogravimetric analysis of (a) pristine mesoporous silica SBA-15, (b) N₃-SBA-15, and (c) DMT-Tr-SBA-15

3.1.5. Nitrogen adsorption–desorption isotherms.

To further investigate the textural characteristics of the as-prepared samples N₂ adsorption–desorption isotherms were measured and displayed Figure. 7. The isotherms indicate that our samples display a type-IV sorption isotherm with a sharp inflection step at P/P₀ ranging from

0.55 to 0.75 typical for OMS [46]. The pore-size distribution, is shown inset the Figure7. The specific surface area, total pore volume, and pore size summarized in Table 2. The pristine OMS display a specific surface area (S_{BET}) around $733.8 \text{ m}^2 \text{ g}^{-1}$, an average pore size (D_p^{BJH}) about 6.81 nm and a pore volume (V_p) about $1.15 \text{ cm}^3 \text{ g}^{-1}$. After azido-silanization, S_{BET} , the V_p and D_p^{BJH} decreased to 375.1 g^{-1} , $0.529 \text{ cm}^3 \text{ g}^{-1}$ and 5.83 nm, respectively. The decrease in S_{BET} is exacerbated after cycloaddition reaction to $276.9 \text{ m}^2 \text{ g}^{-1}$, the D_p^{BJH} was decreased to 5.06 nm, and the V_p was decreased to $0.367 \text{ cm}^3 \text{ g}^{-1}$. This noteworthy decrease in porosity, S_{BET} , and V_p is, may be caused by the partial blockage of the pores, after the grafting of organic groups on SBA-15 inner walls [47].

Figure.7. Nitrogen sorption isotherms at 77 K for the N₃-SBA-15, and DMT-Tr-SBA-15 samples.

Table 2 Summary of Nitrogen Sorption Results

Material	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	D_p^{BJH} (nm) ^a	V_p ($\text{cm}^3 \text{ g}^{-1}$) ^b
SBA-15	733.8	6.81	1.15
N ₃ -SBA-15	375.1	5.83	0.529
DMT-Tr-SBA-15	276.9	5.06	0.367

^aMean pore diameter determined using the BJH method

^bTotal pore volume determined at $P/P^0 = 0.97$

3.2. Adsorption of selected cationic dyes

In order to investigate the selectivity of the as prepared DMT-Tr-SBA-15 hybrid material, we evaluated its performance toward the adsorption of four cationic dyes including rhodamine B (Rhd B), rhodamine 6G (Rhd 6G), methylene blue (MB), and methyl orange (MO) (the molecular structures and chemical properties of the dyes are illustrated in Table (2)). A series of batch adsorption experiment were carried out at room temperature, using the same amount of the adsorbent (30 mg) and in a neutral aqueous solution. For instance, the normalized concentration curve of methylene blue in the liquid phase and solid phase versus contact time with an initial concentration of 40 mg/L and in natural pH solution are plotted in Figure.8. It can be noticing that at the initial adsorption stage, the adsorbent surface contains a lot of available active sites to adsorbate concentration in the liquid phase which led to a significantly increase of the capacity of adsorption q_{eq} . This result is accompanied by a considerable decrease of the intensity of the maximum UV absorption wavelength as displayed Figure 8b for Rhd B. Consequently, a significant evolution of the color of the aqueous solution for both of MB and Rhd B dyes (inset Figure 8a- and 8b). In the second steep, it can be seen after 12 min that the evolution of the capacity of adsorption became slowly till reaching the equilibrium time. This could be due to: (i) a decrease of the dye concentration in liquid phase, (ii) a beginning of the saturation of the available adsorption sites in solid phase, (iii) a combination of these factors [48]. On the other hand, the adsorption rate decreased gradually with increasing contact time and a maximum adsorption of MB was achieved 4.59 mmol g^{-1} at 24 h. Therefore, the minimum contact time of 40 min could be considered for an optimum adsorption of methylene blue.

Table 2. Chemical properties of selected dyes.

Dye	M.W.	UV absorption wavelength (nm)	Type	Molecular structure
MB	319.85	664	Cationic dye
Rhd B	479.01	551	Cationic dye
Rhd 6G	479.01	496	Cationic dye
MO	305.35	466	Cationic dye

Figure 8. Equilibrium adsorption isotherm of MB onto the DMT-Tr-SBA-15 at 25°C; inset shows optical images of dyes solutions MB with the DMT-Tr-SBA-15 adsorbent (a). Temporal evolution of UV-Vis absorption spectra of Rhd B inset shows optical images of dyes solutions Rhd B with the DMT-Tr-SBA-15 adsorbent (b).

In order to study the selectivity of the DMT-Tr-SBA-15 toward the adsorption of these cationic dyes, Figure 9 display the removal efficiency histograms and adsorption capacity of all of selected dyes in the same conditions (30 mg mass of the adsorbent, 40min as equilibrium time and initial dye concentration: 40 mg/L). The capacity of adsorption q_{eq} of for MB, Rhd B, Rhd 6G and methyl orange at the equilibrium time is 4.59, 2.57, 2.3 and 3.7 mmol g⁻¹, respectively. Based on the q_{eq} results, it is clear that the novel adsorbent presents a good removal efficient about 75% and excellent adsorption capacity for all of selected dyes can be attributed to the surface-active sites for adsorption. The adsorption capacity of DMT-Tr-SBA- follows the sequence MB > MO > Rhd B > Rhd 6G. The higher removal efficient for Mb diverted from the high density of negative groups onto adsorbent surface, which induced the favored strong interactions with the positive functional groups of adsorbates.

Figure. 9. Removal efficiency of selected dyes by the DMT-Tr-SBA-15 adsorbent (30 mg) at room temperature with initial dye concentration: 40 mg/L and optimum contact time.

According to above analyses, it is clear that the DMT-Tr-SBA-15 has a good capacity and efficiency for cationic dyes adsorption. To explain this result, Figure. 10 display the structure of the adsorbent which show the presence of the numerous negative active sites for the adsorption process such as Bronsted basic functions, Lewis basic functions and triazole group (nitrogen-donor). In addition to the diversity of active sites, the chemical structure of selected dyes has rich aromatic rings and cationic atoms including S^+ in MB and N^+ in Rhod 6G and Rhod B [49]. These dyes molecules are completely ionized and become positively charged in the solution. Consequently, DMT-Tr-SBA-15 adsorbent is in favor to capture aromatic organic dyes via different ways ; significant π - π interaction electrostatic and anion-cation interaction [50].

Figure. 10. Schematic illustration of the available adsorption sites onto the DMT-Tr-SBA-15 adsorbent.

Conclusion

To sum up, a novel dimethoxytriazine/triazole linked SBA-15 has been synthesized by CuAAC click reaction. Azido-silanization was conducted in order to achieve silica–heterocycles interface with excellent adhesion. An arsenal of techniques (FTIR spectroscopy, XPS, TGA, ^{13}C solid-state NMR N_2 and sorption measurement isotherms) was employed for structural characterization of the hybrid material. Given the strong electrostatic attraction between its negative surface and cationic charges of adsorbates, this novel hybrid was evaluated to remove four selected cationic dyes from aqueous media. The new hybrid material showed high adsorption efficiency, over 75% and a fast removal rate. The adsorption was monitored versus time; the equilibrium was reached within 40 min for a concentration of 40 mg/L. The maximum adsorption capacity for methylene blue at room temperature and natural pH was 4.59 mmol g^{-1} .

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