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# Study of catalytic reduction and photodegradation of methylene blue by heterogeneous catalyst

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#### ARTICLE INFO

#### ABSTRACT

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Keywords: Photodegradation Methylene blue NanoAl-MCM-41 Bleaching Demethylation CoS nanoparticles The photocatalytic degradation of methylene blue is investigated in aqueous solution containing CoS/nanoAl-MCM-41 photocatalyst under visible light. The catalyst is characterized by X-ray diffraction (XRD), UV–vis diffused reflectance spectra (UV–vis DRS) and transmission electron microscopy (TEM) techniques. The effect of CoS, nanoAl-MCM-41 support and different wt% of CoS over the support on the photocatalytic degradation and influence of parameters such as CoS loading, catalyst amount, pH and initial concentration of methylene blue on degradation are evaluated. Hypsochromic effects (i.e. blue shifts of spectral bands) resulting from *N*-demethylation of the dimethylamino group in methylene blue occurs in presence of CoS/nanoAl-MCM-41 under ambient condition. Meanwhile, the bleaching of methylene blue MB, by sulfide ion, in an aqueous solution is studied in the presence nanoAl-MCM-41 catalyst. In the presence of sulfide ions, MB is bleached to its colorless leuco (LMB) and MBH<sub>2</sub><sup>+</sup> forms. In an acidified solution (pH < 2) the bleaching process generates LMB and by changing pH between 2.0 and 7.0 bleaching of MB dye to MBH<sub>2</sub><sup>+</sup> form is observed. Using nanoAl-MCM-41 with encapsulated CoS nanoparticles only causes demethylation of MB in aqueous solution.

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#### 1. Introduction

Methylene blue, MB, is a brightly colored ( $\varepsilon_{664}$  =  $10^5 \, dm^3 \, mol^{-1} \, cm^{-1}$ ) [1], blue cationic thiazine dye, with  $\lambda_{max}$ values [2] at 664, 614 and 292 nm. The use of MB include being an antidote for cyanide poisoning in humans, antiseptic in veterinary medicine and, most commonly, in vitrodiagnostic in biology, cytology, hematology and histology [3]. The reduced forms of MB, leuco-methylene blue, i.e., LMB ( $\lambda_{max} = 256 \text{ nm}$ ), and MBH<sub>2</sub><sup>+</sup>  $(\lambda_{max} = 232 \text{ nm})$  [2,4] are colorless and stable aqueous solutions [5]. The reduction of methylene blue to leuco methylene blue and its re-oxidation have been found to be useful in numerous modern inventions. Used in industry, the colorimetric oxygen indicators are based on the red-ox reaction of methylene blue. The reduction-oxidation properties of MB are provided by the ability of accepting and donating hydrogen ions. The structures and redox reactions relating MB and leuco methylene blue (LMB) and MBH<sub>2</sub><sup>+</sup> are illustrated in Scheme 1. We can take advantage of these properties to treat poisonous chemical substances such as hydrocyanic acid and cyanides, carbon monoxide, nitrites, aniline and its derivatives [6].

As a consequence, different methods are used for reduction of the dyes especially methylene blue dye, Such as chemical methods [7–9], photoreduction methods [4,10–12] and catalytic methods [13–15]. The vast majority of the catalysts developed so far that involve mesoporous silicates (such as MCM-41) are surface-doped with transition metal ions or metal complexes, which act as catalytically active sites. Such doped active sites have proven to be indispensable for reactions with high activation barriers. Moreover, the restricted cavity environment and thus the strong local electric field within the as-synthesized mesoporous materials can be expected to catalyze, as a result of electrostatic activation, some bimolecular redox reactions with slightly unfavorable free energies that do not spontaneously occur in homogeneous solution.

On the other hand, Textile dyes and other commercial colorants have become the focus of environmental remediation efforts because of their natural biodegradability which has become increasingly difficult as a result of improved properties of dyestuffs [16]. Many dyes are highly water-soluble in order to meet the color requirement of deep dyeing. Consequently, traditional wastewater treatment methods such as flocculation, activated carbon adsorption, and biological treatment are considered to be ineffective. Earlier studies [17–20] showed that electron transfer between dyes and nanosized semiconductor particles occurs under visible and UV irradiation, and that dyes can be degraded to smaller organic substances and ultimately mineralized completely to water, carbon dioxide, and other inorganic ions. The data reported recently

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Scheme 1. Schematic depicting the redox mediation of methylene blue.

in the literature on the photocatalyzed degradation of certain dyes by a heterogeneous photocatalytic process are not sufficient for industrial or for large scale pilot plant applications because several experimental parameters (e.g., light intensity, hypsochromic effects, reactor geometry, pH, temperature, concentration and structure of reactant and ...) have complex effects on the degradation reaction and consequently on the treatment costs. On the other hand, N-dealkylation of dyes containing auxochromic alkylamine groups plays an important role in photocatalytic degradation. There are several reports about blue shifts (hypsochromic effects) of the absorption bands during the photooxidative dyes in aqueous semiconductor dispersions under visible or UV light [21-23]. They have resulted that both hypsochromic effects arising from N-dealkylation of dyes and oxidative degradation occur concomitantly under irradiation. The N-demethylation of MB dye is shown in Fig. 1



Fig. 1. Demethylation reaction of MB.

Herein, we examine the photodegradation of MB in aqueous CoS/nanoAl-MCM-41 dispersions under visible light irradiation. The influence of pH, initial concentration of MB, amount of nanocatalyst and amount of semiconductor on the degradative process was studied in detail. We show *N*-demethylation of MB by CoS/nanoAl-MCM-41 under ambient condition. Meanwhile, we report a case where the reduction of methylene blue by S<sup>2–</sup> ions is catalyzed within the nanoAl-MCM-41 pores without the presence of metal ions.

#### 2. Materials and methods

#### 2.1. Reagents and instruments

The nitrate salts of cobalt  $(Co(NO_3)_2)$ , from merck (Darmstadt, Germany), were used as source of metal ions and  $Na_2S \cdot 9H_2O$  (merck, Ouhe, Beijing) was used as source of sulfide ion. Hydrochloric acid and sodium hydroxide were applied for variation of PH of sample solutions. The dye of methylene blue (C.I. name: Basic Blue 9,  $C_{16}H_{18}ClN_3S:3H_2O$ ) was purchased from fluka company (Winchem, Germany).

Powder X-ray diffraction patterns of the samples were recorded using an X-ray diffractometer (Bruker D8 Advance) with Cu K $\alpha$  radiation ( $\lambda$  = 1.54 Å). The UV–vis diffused reflectance spectra (UV–vis DRS) were obtained from UV–vis Scinco 4100 spectrometer with an integrating sphere reflectance accessory. BaSO<sub>4</sub> was used as a reference material. UV–vis absorption spectra were recorded using a shimadzu 1600 pc in the spectral range of 190–900 nm. The transmission electron micrographys (TEM) were recorded with a Philips CM10 microscope, working at a 100 kV accelerating voltage. Samples for TEM were prepared by dispersing the powdered sample in acetone by sonication and then drip drying on a copper grid coated with carbon film.

#### 2.2. Preparation of nanoAl-MCM-41 material

The nanoMCM-41 and nanoAl-MCM-41 materials were synthesized by a room hydrothermal method with some modification in the described procedure in the literature [24]. We used tetraethylorthosilicate (TEOS: Merck, 800658) as a source of silicon and hexadecyltrimethylammonium bromide (HDTMABr; BOH, 103912) as a surfactant template for preparation of the mesoporous material. The molar composition of the reactant mixture is as follows:

#### TEOS: 0.31NaOH: 0.125HDTMABr: 1197H<sub>2</sub>O

The nanoMCM-41 prepared was calcined at 550 °C for 5 h to decompose the surfactant and obtain the white powder. This powder was used as the parent material to prepare nanoAl-MCM-41 free surfactant materials by ion-exchange method with 0.1 M of  $Al_2(SO_4)_3$ ·18H<sub>2</sub>O (Merck) solution. NanoAl-MCM-41 surfactant-free was used for loading the nanoparticles.

#### 2.3. Preparation of CoS/nanoAl-MCM-41 catalysts

The solution 0.1 M of Co(NO<sub>3</sub>) was prepared as precursors of the CoS semiconductor. For ion- exchange, 0.5 g of nanoAl-MCM-41 powder was suspended in 25 mL solution of cobalt nitrate and stirred at room temperature for 5 h. After that, the sample was washed to remove unexchanged Co ions and airdried. Finally, sulphurizing of Co ions was carried out with 0.1 M Na<sub>2</sub>S solution. To make the reaction with the S<sup>2–</sup> ion, 0.5 g of Co<sup>2+</sup>-exchanged mesopore sample was added to 25 mL of 0.1 M Na<sub>2</sub>S solution at a fix temperature and magnetically stirred for 5 h. The sample was washed with deionized water and collected by filtration. The obtained sample fin powder with grey color prepared sample is called CoS/nanoAl-MCM-41. The sample was stable at ambient condition. CoS of 2–20 wt% loading over nanoAl-MCM-41 support is prepared for its photocatalytic evolution.

#### 2.4. Preparation of nanoCoS particles

The major steps involved in this hydrothermal process were carried out as follows: appropriate amount of cobalt salts and Na<sub>2</sub>S were prepared to obtain cobalt sulfide. The mainly synthetic process of CoS was presented as follows:  $0.005 \text{ mol of } Co(NO_3)_2$  was dissolved in 30 mL distilled water and  $0.006 \text{ mol of } Na_2S$  was injected dropwise into this solution with a syringe. Then the solution was placed into a 50 mL Teflon-lined stainless steel autoclave and was filled with about 18 mL ethylenediamine up to 95% of the capacity (50 mL). The autoclaves were sealed carefully and put into an oven maintained at 180 °C for 48 h, then cooled down to room temperature gradually. The precipitates were separated from the aqueous solution and washed with distilled water and absolute ethanol repeatedly. The final products were dried in a vacuum for further characterization.

#### 2.5. The measurement of the degradation efficiency of dye (%D)

The wavelengths absorbance maximum ( $\lambda_{max}$ ) of methylene blue dye is 664 nm. Therefore, photometric analysis of samples before and after irradiation can be used for measurement of the %D (degradation efficiency of dye). The absorption of solution and solid samples was measured by a UV–vis spectro photometer shimadzu model 1600 PC and UV–vis diffused reflectance spectrometer UV–vis DRS Scinco model 4100, respectively. For exploring the effect of pH, the solution's pH was initially adjusted by adding 0.01 M NaOH or 0.01 M HCl and by controlling with a pH meter (Horiba-F12). Before determining optimum pH, the experiments were carried out at the original pH of the dye solution (pH 8).

The percentage of degradation was calculated by using the equation given below:

$$\%D = 100 \times \left[C_0 - \frac{C}{C_0}\right]$$

In which  $C_0$  is the initial concentration of dye and C is the concentration of dye after irradiation in selected time interval.

#### 2.6. Procedures of photodegradation of methylene blue

Photodegrdation experiments were performed with a photocatalytic reactor system. This bench-scale system consisted of cylindrical Pyrex-glass cell with 1.0 L capacity, 10 cm inside diameter and 15 cm height. A 200W tungsten filament Philips lamp  $(\lambda > 400 \text{ nm})$  was placed in a 5 cm diameter quartz tube with one end tightly sealed by a Teflon stop. The lamp and the tube were then immersed in the photoreactor cell with a light path of 3.0 cm. The photoreactor was filled with 25 mL of 0.25–3.2 ppm of dye as pollutant and 0.04-1.2 g/L of CoS/nanoAl-MCM-41 as nanophotocatalyst. The whole reactor was cooled with water-cooled jacket on its outside and the temperature was kept at 25 °C. The reaction solution was continually purged with oxygen and magnetically stirred at least for 15 min before any irradiation. To determine the percentage of dye destruction, the samples were collected at regular intervals, and centrifuged to remove the nanocatalyst particles that exist as undissolved particles in the samples.

In order to obtain maximum degradation efficiency, pH, concentration of dye and amount of photocatalyst were studied in amplitudes of 2–12, 0.25–3.2 ppm and 0.04–1.2 g/L respectively. The experimental were carried out in the presence of CoS nanoparticles in nanoAl-MCM-41 material and for methylene blue dye.

#### 2.7. Reaction of methylene blue with sodium sulfide

In a stoppered cuvette, an aqueous solution of methylene blue (100  $\mu$ M) was mixed with sodium sulfide solution (100 mM) and the final volume of the mixture was maintained to 3 mL. The mixture was shaken well and the absorbance of the solution was monitored at an interval of 2 min. It was found that the absorbance value decreased in  $\lambda_{max}$  = 664, 614 and 292 nm gradually, indicating the progress of the reaction.

In the same way, 2 mg of each nano catalyst (nanoAl-MCM-41 and CoS/nanoAl-MCM-41 materials), was introduced separately into methylene blue solution and was maintained to 3 mL. We also carried out all the reactions in different pH. The pH solution is adjusted by adding HCl or NaOH. In all cases the reaction was monitored spectraphotometrically at the dye  $\lambda_{max}$  at 664 nm.

#### 3. Results and discussion

#### 3.1. Characterization of CoS nanoparticles in nanoAl-MCM-41

The XRD pattern of nanoAl-MCM-41 support, CoS/nanoAl-MCM-41 and nanoCoS loading on the support are shown in Fig. 2.

Measurements of the samples were carried out in different  $2\theta$  range, under the condition of 40 kV and 40 mA, at a step size of  $2\theta = 0.02^{\circ}$ . The XRD patterns of nanoAlMCM-41 show typical characteristic three-peak pattern with a very strong one at a low  $2\theta$  and two peaks at higher  $2\theta$  values [24,25]. The XRD pattern of CoS/nanoAl-MCM-41 is similar to nanoAl-MCM-41 sample (Fig. 2A). However, some differences, such as the boarding of the diffraction peaks, decrease of some peaks intensity as well as the shift to the peak positions to the lower angle can be observed in the spectra. With limiting the range to  $2\theta = 25-45^{\circ}$ , two peaks are observed (Fig. 2B) approximately at  $2\theta$  equal  $31^{\circ}$  and  $46.5^{\circ}$ , which are due to the reflection of the ~ $30.5^{\circ}$  (100) and ~ $46^{\circ}$  (101) planes, in the nanoCoS phase, respectively [26]. These shifts of the peak position to the slightly lower angles are in agreement with the reports made for other molecular sieves [27–29].



**Fig. 2.** (A) X-ray diffraction patterns of the (a) nanoAl-MCM-41 and (b) CoS/nanoAl-MCM-41 (B) X-ray diffraction pattern of nanoCoS. Inset shows X-ray diffraction pattern CoS/nanoAl-MCM-41 sample.

The XRD patterns of nanoAl-MCM-41 and CoS/nanoAl-MCM-41 were used for evaluating the approximate size of support and CoS nanoparticles. The support size was obtained about 15–20 nm using Debye-Scheerer formula and based on the full width maxima (FWHM) of X-ray diffraction pattern. In the same way, the average size of CoS nanoparticles was about 10 nm.

To ascertain the capability of each particular composite material to photodegradation organic chemicals in the visible range of spectrum, one needs to analyze the UV–vis diffuse reflectance spectra (Fig. 3). This allows us to observe the absorption in visible parts of the spectrum. Fig. 3 shows that both can be used as efficient photocatalysts under visible light irradiation (absorption edge of 400–500 nm). But nanoCoS sample shows high turbidity that decreases the radiation flux. The use of mesoporous supported semiconductor has allowed the enhancement of photodegradation rate in comparison with neat semiconductor [30]. Spectrum indicates that nanoAl-MCM-41 is not suitable material for degradation of dye under visible light since it has absorption edge lower than 400 nm.

Transmission electron microscopy along with the textural properties of the samples discussed above bring us important information regarding whether the CoS particles are located inside or outside the pore structures used in this work. TEM images of samples are shown in Fig. 4. Even darker images have been obtained on nanoAl-MCM-41 reference indicating that the dark aspect can be associated with the presence of water trapped inside Al-MCM-41 grains. The image of CoS/nanoAl-MCM-41 sample reveal information of CoS nanoparticles aggregation on the surface of mesoporous material. The particle size of nanoAl-MCM-41 observed from TEM photographs is around 15 nm and no change in the particle size of nanoAl-MCM-41 is observed on modification with CoS.

The BET results show that, the pore volume of the host materials, which was  $1.2 \text{ mL g}^{-1}$  for nanoAl-MCM-41, increased to  $1.4 \text{ mL g}^{-1}$  for CoS/nanoAl-MCM-41. The specific surface areas of the



Fig. 3. Diffuse reflectance spectra for the set of nanoCoS samples and Al-MCM-41 sample.

nanocomposite CoS/Al-MCM-41 was increased from 1025 m<sup>2</sup> g<sup>-1</sup> for nanoAl-MCM-41 to 1228 m<sup>2</sup> g<sup>-1</sup> for CoS/nanoAl-MCM-41. It is apparent that the high surface area CoS/nanoAlMCM-41 plays a special role in these visible light photocatalysis.

## 3.2. Photodegradation of methylene blue dye using CoS/nanoAl-MCM-41 material

The time dependent electronic absorption spectrum of methylene blue dye during photo irradiation is presented in Fig. 5. The reaction solution was purged with oxygen and stirred at least for 15 min before any radiation. After 30 min of irradiation under visible light in a CoS/nanoAl-MCM-41 suspension, 95% of dye was decomposed and decolorization of solution was observed. Besides, no new bands appear in the UV-vis region due to the reaction intermediates formed during the degradation process.

The effects of visible irradiation, nanoCoS and nanoAl-MCM-41 material on photodegradation of methylene blue are shown in Fig. 6. This Figure indicates that in the presence of mixed photonanocatalyst (17%CoS/nanoAl-MCM-41) and visible irradiation, 95% of dye degraded at the irradiation time of 30 min while it was 51% for nanoCoS (without nanoAl-MCM-41) visible irradiation. It is 19.3% degradation for the same experiment performed in the absence of nanoCoS and 5% degradation in the absence CoS/nanoAl-MCM-41. These experiments demonstrated that both visible light and a photocatalyst, are needed for the effective degradation of methylene blue.

This is due to the fact that when nanoCoS is illuminated with the visible light, electrons are promoted from the valence band to the conduction band of the semiconducting oxide to give electron–hole pairs. The valence band ( $h_{VB}$ ) potential is positive enough to generate hydroxyl radicals at the surface and the conduction band





Fig. 4. Transmission electron micrograph of (a) nanoAl-MCM-41 and (b)  $17\,wt\%$  CoS/nanoAl-MCM-41 catalyst.



**Fig. 5.** Spectra change that occur during the photocatalytic degradation of aqueous solution of methylene blue: pH 7,  $[17 \text{ wt\% CoS/nanoAl-MCM-41}] = 0.8 \text{ g/L}, C_0 = 0.32 \text{ ppm}.$ 



**Fig. 6.** Effect of visible light and different photocatalyst on photocatalytic degradation of methylene blue.  $C_0 = 0.32$  ppm, [17 wt% CoS/nanoAl-MCM-41] = 0.8 g/L, pH 7.

 $(e_{CB})$  potential is negative enough to reduce molecular oxygen. The hydroxyl radical is a powerful oxidizing agent and attacks organic pollutants present at or near the surface nanoCoS. It causes photooxidation of dye according to the following reactions [31]:

$$\cos h\nu \rightarrow \cos(e_{\rm CB}) + \cos(h_{\rm VB})$$

 $h_{\rm VB} + H_2 O_{(ads)} \rightarrow H^+ + {}^{\bullet}OH_{(ads)}$ 

 $h_{\rm VB} + {\rm OH^-}_{(ads)} \rightarrow \ ^{\bullet}{\rm OH}_{(ads)}$ 

$$e_{\rm CB} + O_{2(\rm ads)} \rightarrow {}^{\bullet}O_2^{-}_{(\rm ads)}$$

 $OH_{(ads)} + dye \rightarrow degradation of the dye$ 

To understand the role of support during the photocatalytic degradation of methylene blue, the amount of nanoCoS available over 17 wt% nanoCoS supported system is considered for the degradation activity and the studies are carried out using 0.8 g/L catalyst in 0.32 ppm methylene blue. From Figs. 5 and 6, it is observed that CoS/nanoAl-MCM-41 system is showing higher rate of degradation than nanoCoS or nanoAl-MCM-41 alone. This is due to the higher adsorption capacity and also OH radicals' availability. It is apparent that the high surface area CoS/nanoAl-MCM-41 plays a special role in better photodegradation. Meanwhile, high surface area causes higher adsorption capacity and also OH radicals' availability [32,33]. On the other hand, nanoCoS, produced high turbidity that decreases the radiation flux and causes low degradation.

#### 3.3. Effect of variables influence on degradation efficiency

#### 3.3.1. Effect of nanocatalyst amount

In order to determine the optimal amount of photocatalyst, some experiments were performed at pH 8 by varying the amount of catalyst from 0.04 to 1.2 g/L. The effect of catalyst amount on the rate of degradation is shown in Table 1.

As seen, the optimum nanocatalyst amount for degradation of methylene blue dyes is 0. 8 g/L. It is observed that rate increases with increase in catalyst amount from 0.04 to 1.2 g/L. This is probably due to increase in the number of CoS nanoparticles, that increases the number of photons and dye molecules absorbed. Increase of the catalyst amount more than 0.8 g/L results in the decrease of degradation rate. This phenomenon may be explained by aggregation of CoS nanoparticles at high concentrations causing a decrease in the number of surface active sites and increase

Table T					
Variable	influence	on de	gradation	of effici	ency.

Variables	D%	
Photocatalyst amount(	g/L)	
0.04	70	
0.2	75	
0.4	90	
0.8	98	
1.2	89	
Supported photocataly	st amount (wt%)	
3	70	
5	74	
10	80	
17	98	
20	80	
Dye concentration (pp	n)	
0.25	88	
0.28	92	
0.32	98	
0.5	94	
1.5	89	
3.2	85	

in opacity and light scattering of CoS nanoparticles at high concentration, load to decrease in the passage of irradiation through the sample.

#### 3.3.2. Effect of the composition of the supported photocatalyst

The effect of CoS loading on nanoAl-MCM-41 material is investigated with 2–20 wt% content and the results are depicted in Table 1.

The effective decomposition of methylene blue after 120 min irradiation time was observed when the photocatalyst contained 17 wt% CoS, prepared by using ion-exchange method. For comment of this result, we propose that the hydroxyl radical on the surface of nanoparticle CoS is easily transferred onto the surface of nanomesoporous material. This means the organic pollutants, which have already been adsorbed on the mesoporous materials, have a chance to be degraded due to the appearance of hydroxyl radical, resulting in the enhancement of photodegradation performance of CoS/nanoAl-MCM-41. Experimental results show that about 17 wt% of CoS provides the best condition for achieving synergism between CoS and nanoAl-MCM-41. The enhanced phtocatalytic activity over the composite CoS/nanoAl-MCM-41 is reflecting the beneficial adsorption properties of nanoAl-MCM-41. If decrease the CoS in composition of photocatalyst (less than 17 wt%) the rate of production reaction of the hydroxyl radical by CoS under visible irradiation is not enough to react with all the molecules of dye that are absorbed on the surface of nanoAl-MCM-41 and if increase the CoS in composition of photocatalyst, the adsorption ability of nanoAlMCM-41 in comparison with the rate of production reaction of hydroxyl radical with CoS under visible irradiation decrease.

#### 3.3.3. Effect of concentration of dyes

The degradation efficiency of dye decreased with increasing the initial concentration of dye to more than 0.32 ppm. The results are shown in Table 1. The decrease of %D with increase of concentration of dye can be due to two reasons. With increasing the amounts of dye, the more of dye molecules will be adsorbed on the surface of the photocatalyst and the active sites of the catalysts will be reduced. Therefore, with increasing occupied space of catalyst surface, the generation of hydroxyl radicals will be decreased. Also, increasing concentration of dye can lead to decreasing the number of photons that arrive to the surface of catalysts. The more light is adsorbed by molecules of dye and the excition of photocatalyst particles by photons will be reduced. Thus, photodegradation efficiency diminished [34].



**Fig. 7.** Change in decomposition% aqueous solution of methylene blue as a function of pH: [17 wt% CoS/nanoAl-MCM-41] = 0.8 g/L, C<sub>0</sub> = 0.32 ppm.

#### 3.3.4. Effect of pH in photodegradation

Photodegradation of dye (0.32 ppm) was studied in amplitude pH of 2.0–12 in the presence of CoS/nanoAl-MCM-41 catalyst (0.8 g/L). The results for irradiation time of 30 min are shown in Fig. 7. In all cases, the maximum degradation efficiency was obtained in alkaline pH 8 for methylene blue. In presence of CoS/nanoAl-MCM-41 and in pH 9, 98% of degradation efficiency is obtained. The surface of photocatalyst is probably positively charged in acidic solutions and negatively charged in alkaline solutions. As a result, it is not surprising to observe increase in the adsorption of dye molecules (with positive charge) on the surface of photocatalyst in alkaline solutions and thus the increase in the degradation efficiency of dye [35].

A low pH is associated with a positively charged surface which cannot provide hydroxyl groups needed for hydroxyl radical formation. On the other hand, higher pH value can provide higher concentration of hydroxyl ions to react with the holes form hydroxyl radicals [36]. But, the degradation of dye is inhibited when the pH value is so high (pH>8) because the hydroxyl ion compete with dye molecules in adsorption on the surface of photocatalyst [37].

In other words, at low pH, the adsorption of cationic dyes on the surface of photocatalysts decreases because the photocatalysts surface is positively changed and repulsive forces are due to decreased adsorption. Thus, the degradation efficiency will be decreased in acidic pH.

#### 3.4. Demethylation and bleaching of MB by sulfide ion

The reports and above results show that MB be photodegraded under UV or visible light [4,38,39]. But methylene blue can be bleached in ambient condition [7,13,14]. We observed that sulfide ions reduce methylene blue to LMB and  $MBH_2^+$  forms in aqueous and nanoAl-MCM-41 solutions. The bleaching of MB color by S<sup>2–</sup> in presence of nanoAl-MCM-41 can be explained with the concepts of encounter probability [40] and the fractal nature of the nanoAl-MCM-41 material surface [41].

Since the redox potential of dyes (like NMB, MB) in the solution phase is strongly dependent on the pH, thus, the study of influence of pH on the bleaching dye is very important. The bleaching of methylene blue dye (100  $\mu$ M) was studied in amplitude pH of 2–12 in the presence of nanoAl-MCM-41 catalyst (0.66 g/L). The absorption spectra methylene blue dye after reaction with S<sup>2–</sup> ion (100 mM) in presence of nanoAl-MCM-41, in different pH, is shown in Fig. 8. The results indicated that at 2 < pH < 7, MB is reduced to MBH<sub>2</sub><sup>+</sup> form (Fig. 8a). Because absorption values increase at wavelength 232 nm and they decrease at 660, 614 and 292 nm. This increase of the absorption peaks is in agreement with other



**Fig. 8.** UV-vis spectra for the reduction of MB to (a)  $MBH_2^+$  by  $S^{2-}$  in 2 < pH < 7 (b) LMB by  $S^{2-}$  in pH < 2 (c)  $MBH_2^+$  and thionine by  $S^{2-}$  in pH > 7. Conditions: [MB] = 100  $\mu$ M, amount of nanoAl-MCM-41 = 0.66 g/L.

reports [7,42]. Fig. 8b shows two peaks at 322 and 256 nm. These peaks were produced at pH < 2 and they are related to reduction of MB to LMB form in presence of sulfide ion. LMB form is reported by other researchers [43,44]. Neutralization of amines in MB molecules with strong acid takes place at low pH (pH < 2) i.e. the amines are rendered ineffective as electron donors. That is why we observe reduced form of LMB for MB dye at pH < 2. But when pH is between 2–6, amines act as electron donors and MB molecule reduces to  $MBH_2^+$  form [45].

The demethylation of MB occurs under irradiation [21,23] or in alkaline median [46]. We observed reduction of methylene blue to  $MBH_2^+$  form and demethylation it at pH above 7 after reaction with  $S^{2-}$  ion (Fig. 8c). Fig. 8c indicates increase at intensity of absorption peak in wavelength 232 nm. This peak related to reduction of MB to  $MBH_2^+$  form. On the other hand, the peaks are disappeared at wavelength 664 and 614 nm but a new peak is observed



Fig. 9. UV-vis spectra for the demethylation of MB to thionine in presence of CoS/nanoAl-MCM-41 catalyst. Conditions: [MB] = 100  $\mu$ M, amount of CoS/nanoAl-MCM-41 = 0.66 g/L, pH 6. Inset: UV-vis spectra at range 500–700 nm.

at wavelength 604 nm. Absorption band at 604 nm is related to thionine dye [44,47]. In fact, methylene blue dye is demethylated completely at pH above 7. Meanwhile, the color of MB solution becomes less intense when all of the auxochromic groups (methyl or methylamine) degrade.

## 3.5. Reaction between MB and CoS/nanoAl-MCM-41 in ambient condition

We also studied the effect of incorporated CoS nanoparticles on MB dye. Methylene blue is demethylated in presence of CoS/nanoAl-MCM-41 (Fig. 9). We deduced that the CoS nanoparticles are responsible for demethylation of MB. This is due to the fact that when CoS is illuminated with indoor lighting, electrons are promoted from the valence band to the conduction band of the semiconducting oxide to give electron-hole pairs. Electron-hole pairs produce hydroxyl radical for degrading dyes [21,48,49]. The greater reactivity is attributed to a space constriction effect, with resultant enhanced electric fields, associated with the close fit of the CoS/nanoparticles in the nanomesoporous of Al-MCM-41 would severely diminish the space available to the reactants.

#### 4. Conclusion

In this work we have reported that CoS/nanoAl-MCM-41 is an effective photocatalyst for degradation of methylene blue under visible light. The results showed that pH is one of the main effecting factors in degradation of dye and the optimum pH was obtained about 9. Meanwhile, we have observed that MB only is demethylated in presence of CoS/nanoAl-MCM-41 catalyst without visible light. In the continue we have shown reduction of the cationic dye MB by S<sup>2–</sup> ion in aqueous solution and nanoAl-MCM-41 catalyst under the ambient conditions. The rate of reduction in presence of nanoAl-MCM-41 catalyst is more than that without nanomesoporous catalyst. Reduction of MB depends on solution pH. At low pH (pH 2), MB reduces to lecuo methylene blue (LMB) and at pH 6 methylene blue reduces to MBH<sub>2</sub><sup>+</sup> form. At high pH (pH 8), MB shows two processes: reduction to MBH<sub>2</sub><sup>+</sup> form and demethylation. MB turns into thionine dye when it demethylates.

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