



## Comparative study of different systems for adsorption and catalytic oxidation of hexamine in industrial wastewaters



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### ABSTRACT

This work reports adsorption and catalytic oxidation process for degradation of hexamine (HMT)-containing industrial wastewater based on the reduction in total organic carbon. The studied systems include hydrogen peroxide, MCM-41, phosphotungstic acid (PTA)/MCM-41 embedded via impregnation method, PTA/H<sub>2</sub>O<sub>2</sub> and PTA/MCM-41 embedded via impregnation or direct synthesis methods in the presence of hydrogen peroxide. The TOC results indicated that the system including PTA embedded within MCM-41 via direct synthetic method in the presence of H<sub>2</sub>O<sub>2</sub> has a higher performance for degradation of HMT-containing wastewater. The total organic carbon for the mineralization of HMT was obtained to be 57%, under optimum conditions.

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### 1. Introduction

The treatment of industrial effluents is a challenging topic in environmental sciences and control of water pollution has become increasing importance in recent years [1]. Many efforts have been performed to develop technologies that are capable to reduce the hazardous materials resulted from the industrial activities. Among the many cases, development of processes to transform the toxic and hazardous pollutants into less toxic compounds is one of the most effective solutions [2]. With this objective, many processes have been developed over recent years [3–9]. Hexamine (HMT)-containing waste streams are introduced as highly resistant to treatment [3]. Hexamine, (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>, is a non-aromatic heterocyclic compound with a symmetrical three-dimensional molecular structure, as shown in Fig. 1. In acidic condition, it can be hydrolyzed to formaldehyde and ammonia [4].

HMT-containing waste must be considered as a real wastewater pollutant. Therefore, HMT and its derivatives must be removed from wastewaters and it should not be allowed to enter into water resources and soils. However, there are few reports to remove or demineralize of HMT. The use of physicochemical separation and chemical reaction methods have been investigated for treatment of HMT-containing waste. It has been studied that cellulose acetate

membranes can be used to separate hexamine wastewater [5]. Nevertheless, these physicochemical separation methods only transfer pollution from one phase to another phase without decreasing their pollution [6].

Moreover, the traditional Fenton process, one of the advanced oxidation processes (AOPs), is widely used as a suitable treatment method for highly concentrated wastewaters due to its effectiveness in the production of hydroxyl radicals [7,8]. Fenton's oxidation method is based on the use of mixture of hydrogen peroxide and iron salts (Fe<sup>2+</sup>) which produces hydroxyl radicals (OH<sup>•</sup>) at acidic pH in ambient conditions. Advantage of this method is the Fenton's reagent is not necessary energy input to activate H<sub>2</sub>O<sub>2</sub>. One of the drawbacks for Fenton's method is the production of significant amount of ferric hydroxide sludge that needs further separation and disposal. The previous experimental results have indicated that only applying the Fenton process is not enough to treat HMT wastewater [3]. Therefore, a novel Electro-Fenton (EF-Fere) method has been investigated using H<sub>2</sub>O<sub>2</sub> and electro-generated ferrous ion for treating HMT-containing wastewater [3,9]. The results have shown that the EF-Fere method was the most efficient. Although, the EF-Fere method has the high capacity for wastewater treatment, it requires most complicated equipments.

Catalytic oxidation methods due to their capacity to convert dangerous toxic pollution to environment friendly compounds are recently interested [10,11]. The PTA (phosphotungstic acid) as HPA (Heteropoly acids) source has been used for catalytic oxidation.

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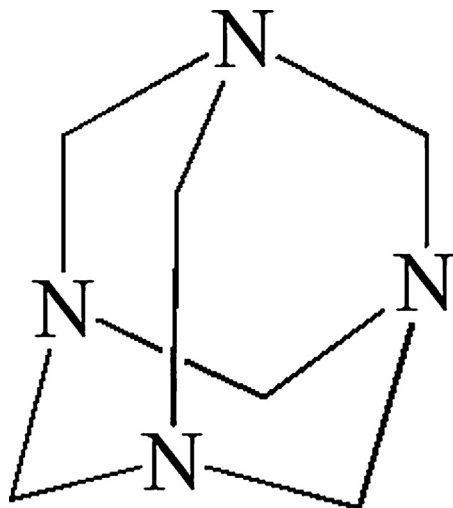


Fig. 1. The molecular structure of HMT.

Advanced oxidation processes based on HPA have shown high efficiency in destroying several organic compounds [12,13]. Heteropoly acids with Keggin anion structures have received considerable attention due to unique ensemble of properties, including inorganic nature, metal oxide-like structure, thermodynamic stability to oxidation, thermal and hydrolytic stability, tunable acidities, redox potentials, etc. [14,15]. Phosphotungstic acid has been applied as acid, oxidative and bifunctional catalysts in homogeneous or heterogeneous phases [16,17], due to its high acidic strength and relatively high thermal stability. Many efforts have been made to improve the catalytic activity of HPA. Despite the advantages, there exist some drawbacks about catalysis with HPA based systems include high solubility in polar solvents causing separation problems and low surface area which is an important restriction for the catalytic systems. All these limitations may be satisfied by grafting HPA within proper heterogenizing supports, which can be a great step to extending catalytic applications of HPA based catalysts [15]. The properties of HPAs were kept up in the step of engaging HPAs into porous materials without dissolution or elution. Furthermore, MCM-41 has been considered special tendency due to its potential use in adsorptive separations and catalytic conversion of large molecules. MCM-41 possesses a regular hexagonal array in its mesoporous structure with a high surface area, specially adsorption capacities and unique catalytic properties [18].

In this work, an efficient adsorption and destruction process has been developed to reduce TOC of the HMT-containing wastewater. The main objective of this study is assessment of different processes efficiency in adsorption and degradation of the HMT-containing wastewater. The various systems such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), MCM-41, PTA embedded within MCM-41 via impregnation method (PTA/MCM-41), PTA/ $\text{H}_2\text{O}_2$  and PTA within MCM-41 via impregnation and direct synthetic methods in the presence of  $\text{H}_2\text{O}_2$  were studied and compared. The total organic carbon (TOC) has been determined in order to evaluate the mineralization rate, as an important indicator of treatment effectiveness.

## 2. Experimental

### 2.1. Materials

All chemicals used for direct synthesis of PTA-encaged MCM-41 such as sodium tungstate dihydrate ( $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ) and disodium hydrogen phosphate dodecahydrate ( $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ) were obtained from Merck Company (Germany). Analytical grade of

methyl orange (MO) and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was purchased from Aldrich. Doubly distilled water was used for preparation of all aqueous solutions. The materials used for the synthesis of mesoporous molecular sieve and MCM-41 were ammonia solution ( $\text{NH}_4\text{OH}$ , 30 wt.%, Sigma–Aldrich Chemical Co.), hydrochloric acid solution (HCl, 37 wt.%, Samchun Pure Chemical Co., Ltd.), sodium silicate solution (14 wt.% NaOH, 27 wt.%  $\text{SiO}_2$ , Sigma–Aldrich Chemical Co.) as a silica source, cetyltrimethylammonium chloride solution (CTAC, 25 wt.% solution in water, Aldrich Chemical Co., as the surfactant, and sodium fluoride (NaF, 99.8%, Sigma–Aldrich Chemical Co). Keggin structured, phosphotungstic acid,  $\text{H}_3(\text{PW}_{12}\text{O}_{40}) \cdot n\text{H}_2\text{O}$ , obtained from Merck (Germany) was used as HPA source for conventional impregnation method and as catalyst on the degradation of the HMT-containing wastewater.

A stock standard solution of  $\text{H}_2\text{O}_2$  ( $3.3 \times 10^{-4} \text{ mol L}^{-1}$ ) was prepared from 30%  $\text{H}_2\text{O}_2$  solution and standardized by titration with  $\text{KMnO}_4$ . The freshly prepared solutions were stored in an amber-glass bottle in refrigerator ( $4^\circ\text{C}$ ) prior to the experiments.

### 2.2. Apparatus

The FT-IR spectra were recorded on a Shimadzu FT-IR 8400s spectrophotometer. The surface morphology of the sorbents was examined using scanning electron microscopy (SEM). Scanning electron micrographs were recorded using on a SEM-JXA, 840 series instrument using a gold film for loading the dried particles on the instrument. Gold films were prepared by a sputter coater model SCD005 made by BAL-TEC (JEOL Japan). TOC measuring was performed with a Shimadzu 500-TOC. The spectrophotometric measurements were carried out with a Cintra 101 spectrophotometer (GBC Scientific Equipment, Australia). A digital pH meter, Metrohm model 691, equipped with a combined glass calomel electrode was used for the pH adjustments.

### 2.3. Preparation of hexamine-containing wastewater

Wastewater samples were obtained from a chemical industrial plant of HMT production located in Iran (Sina Chemical Industries Co.). The characteristics of this high strength HMT-containing stream are listed in Table 1.

All the samples were prepared freshly prior to analysis. Stock solutions of Hexamine-containing wastewater were collected directly from the production-line and then, diluted by doubly distilled water (DDW). Hexamine-containing wastewater solutions of initial concentration (50 ppm) were prepared by diluting the stock solution (2000 ppm) in appropriate proportion. The initial pH of wastewater samples was about 8.5–9.0. The pH of all solutions was adjusted by aqueous solutions of HCl (0.1 M) and NaOH (0.1 M).

### 2.4. MCM-41 synthesis

The synthesis of MCM-41 was carried out according to the literature [19]. For this purpose, aqueous solution of CTAC (25 wt.%) as the surfactant, sodium silicate solution (14 wt.% NaOH, 27 wt.%  $\text{SiO}_2$ ) as a silica source, aqueous HCl solution (37 wt.%),  $\text{NH}_4\text{OH}$  solution (30 wt.%) and NaF in doubly distilled

Table 1  
Characterization of the hexamine-containing wastewater used in the study.

pH	COD <sup>a</sup>	Conductivity <sup>b</sup>	Hexamine <sup>a</sup>	Formaldehyde <sup>a</sup>	$\text{NH}_3^{\text{a}}$
8.5	15,800	9.4	3100	1000	400
8.9	18,350	9.9	5820	1200	650

<sup>a</sup> ( $\text{mg L}^{-1}$ ).

<sup>b</sup> ( $\text{mho cm}^{-1}$ ).

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