Advances in Environmental Technology 4 (2017) 243-248

Advances in Environmental Technology

journal homepage: http://aet.irost.ir

Sonocatalysis degradation of methyl orange using zinc sulfide carbon nanotubes nanocatalyst

Mohammad Reza Rezaei Kahkha[1*] Batool Rezaei Kahkha[2] and Ali Faghihi- Zarandi[2]

[1]*Department of Environmental Health Engineering, Zabol University of Medical Sciences, Zabol, Iran.*

[2]*Department of Occupational Health Engineering, Kerman University of Medical Sciences, Kerman, Iran.*

ARTICLE INFO

Article history:
Received 7 February 2018
Received in revised form
14 May 2018
Accepted 16 May 2018

Keywords:
Nanocatalyst
Sonocatalysis
Degradation efficiency
Methyl orange
Zinc sulfide
Carbon nanotubes

ABSTRACT

Dye sewage is dangerous problem in our environmental aquatics that cause generation of harmful effects for living organism. In this work, because of simplicity, easy operation, high efficiency and no creating secondary pollutants, ultra sound radiation applied for degradation of a synthetic dye, methyl orange using zinc sulfide nano particles decorated on carbon nanotubes as nanocatalyst. ZnS/CNTs prepared by co-precipitation of carbon nanotubes and zinc aceate. Methyl orange (MO) is a cationic dye that used widely in some medical uses, coloring paper, dyeing cottons, wools, coating for paper stocks and etc. For achieving highest degradation efficiency several parameters such as pH, amount of nanocatalyst, initial dye concentration and time were evaluated and optimized. Results showed that highest degradation efficiency (100%) obtained at 0.3 gr of nanocatalyst while initial dye concentration is 30 mg/L at pH, 2. Comparison of several methods for degradation of methyl orange showed feasibility of applied method. In addition, reusability of nanocatalyst was suitable for degradation of MO in real wastewater samples.

1. Introduction

Dye sewage is most concerning problem in our environmental aquatics that cause generation of harmful effects for living organism [1,2]. Dyes strongly inhibit penetration of light in to water ecosystems and consequently reduce photosynthesis [3]. Because of chemical and biological stability, convential sewage treatment process and natural systems cannot treated these types of pollutants [4]. Therefore, advanced treatment methods are needed for removal of dye materials. In this regard, Advanced Oxidation Process (AOP) is considered as one of promising methods for degradation and elimination of dyes and other emerging pollutants [5,6]. Ozonation, photocatalysis by aid of semiconductors, Fenton and Ultrasonic methods are examples of AOPs process [7,8,9]. Among them, Ultra Sonic (US) has become attractive process for removal of organic pollutants because of its simplicity, easy operation, high efficiency and also no creating secondary pollutants [10]. US degradation use of acoustic cavitation through ultrasonic irradiation and subsequent production of high energy radicals such as OH° and other reactive radicals that oxidized organic matters [11]. These processes are time and energy consuming that requires a large amount of hydroxyl radicals. For overcome at this problem semiconductor substant such as Tio_2, ZnO, CdS and ZnS were used. Sonocatalysts provides more cavity nucleation sites that produce additional radicals group [12,13]. Zinc sulfide (ZnS) has band gap energy of 3.6 eV that makes its applicable for studying of photocatalytic, sonocatalytic and as quantum dots activity [14]. Various methods have been reported to increase the catalytic activity of ZnS such as semiconductor coupling, metal doping, non-metal doping and immobilization of ZnS on the materials surface with large surface area [15]. Carbon Nanotubes (CNTs) are one of most studied nano particles in separation and elimination of pollutants from water and wastewater solutions. Unique properties of CNTs such as large surface area, thermal and chemical stability make its useful as electrochemical sensor, adsorbent in separation science and other application that reported in past decade [16]. Methyl orange (MO) is a cationic dye that used widely

*Corresponding author. Tel: +985432232190
E-mail address: m.r.rezaei.k@gmail.com
DOI: 10.22104/AET.2018.2766.1135

in some medical uses, coloring paper, dyeing cottons, wools, coating for paper stocks, etc. Though MO is not strongly hazardous, it can cause some harmful effects. Acute exposure to MO will cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice and quadriplegia and tissue necrosis in humans [17]. Under ultra sound irradiation, possible reactions were occurred between ultra sound radiation, ZnS, CNT and methyl orange [16]:

$$ZnS/CNT + US \rightarrow e^- + h^+ \quad (1)$$

$$2e^- + O_2 + 2H^+ \rightarrow H_2O_2 \quad (2)$$

$$H_2O_2 \rightarrow 2OH^0 \quad (3)$$

$$h^+ + H_2O \rightarrow OH^0 \quad (4)$$

$$MO + OH^O \rightarrow \text{intermediate molecules} \rightarrow CO_2 + H_2O \quad (5)$$

In this research, ZnS nanoparticles were synthesized and immobilized on Multiwalled carbon nanotubes and used for degradation of methyl orange from aqueous solutions. Effect of several parameters that influences removal efficiency such as pH, amount of nanocatalyst, initial dye concentration and time of degradation were studied and optimized.

2. Material and methods

All chemicals were of analytical grade. Multiwalled carbon nanotubes (outer diameter of 5–20 nm, inner diameter of 2–6 nm, length of 1–10 µm, purity ≥95 %) were purchased from Plasmachem, Germany. Stock solution was prepared by dissolving 1.0 g of MO in 1000 mL distilled water without further purification. Analysis of methyl orange was performed by CECIL spectrophotometer (CECIL, England) at wavelength of maximum adsorption at 664nm.UltraSonic degradation was done using ELMA ultrasonic bath (ELMA, Germany).

2.1. Synthesize of adsorbent

Synthesize of ZnS/CNT nanocatalyst was similar to our previously reported work [18]. Briefly, 0.4 gr sodium sulfide hydrate was added to a suspension of CNT that made by ultrasonication of 100 mg powdered CNT in 100 ml absolute ethanol. 1.24 gr zinc acetate added to 8.36 ml manganese acetate solution and diluted to 100 ml. This solution added drop by drop to first solution for 30 minutes and formed nanocatalyst was dried in an oven at 60 °C Characterization of this synthesized nano catalyst are similar to those we already reported [18].

2.2. *Sonocatalytic degradation procedure*

0.3 gr of ZnS/CNTs nanocomposite were introduced in 250 ml Erlenmeyer's containing 20 mg/L methyl orange. This solution sonicated with a frequency of 60 KHz and output power of 240 W in acidic pH for a specified time. After this remained methyl orange was measured with spectrophotometer.

3. Results and discussion

For enhance degradation efficiency of MO with ZNS in this sonocatalytic process we tried to obtain optimized condition. Several parameters including, pH, initial concentration of dye, amount of ZnS and time were tested and optimized.

3.1. Effect of pH on degradation efficiency

pH is one of most important factor in degradation study of dyes. For evaluation effect of pHs between 2-9 were studied and optimized. Figure 1 showed that highest degradation efficiency obtained at pH between 2 to 4 with percent removal about 96%. Hence, pH, 2 was selected as optimized pH for subsequent experiments.

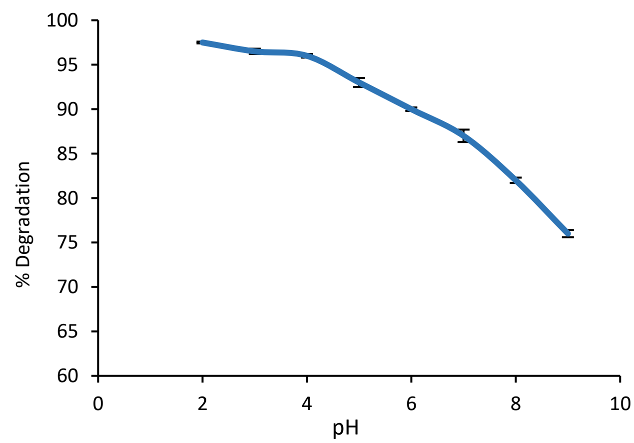

Fig. 1. Effect of pH on degradation efficiency. (Experimental conditions: amount of ZnS/CNTs: 0.5 gr, initial dye concentration: 30 mg/L, contact time: 2 min)

3.2. Effect of amount of ZnS/CNTs on removal efficiency

Amount of catalysis is one of most important parameters on AOP processes. Increasing adsorbent dose provided more electron and hole and subsequent producing of hydroxyl radicals. For investigation of this parameter 0.1 to 1 gr of ZnS/CNTs nanocatalyst was used. Figure2 showed that, with increasing of nanocomposite dosage, removal percent of MO increased. Highest removal efficiency was obtained at 0.3 gr of nanocatalyst and after this point removal percent of MO was decreased.

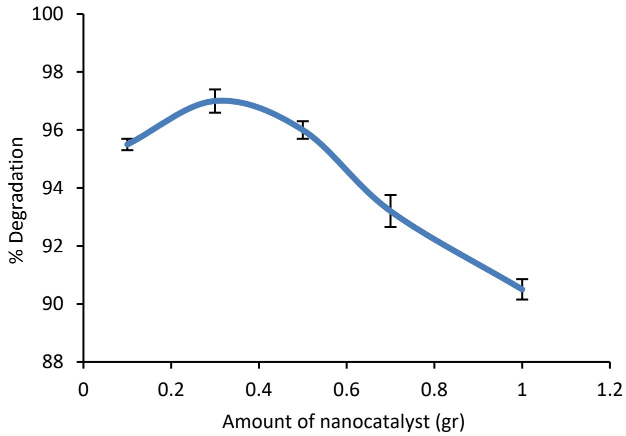

Fig. 2. Effect of amount of ZnS/CNTs on degradation efficiency. (Experimental conditions: pH: 2, initial dye concentration: 30 mg/L, contact time: 2 min)

3.3. Effect of initial concentration of dye on degradation efficiency

For achieving best percent removal of MO with ZnS/CNTs nanocatalyst, we examined initial concentration of methyl orange between 20 to 70 mg/L while contact time is 2 minutes and amount of nanocatalyst was 0.3 gr. Results are depicted in Figure 3 As shown in Figure 3 best removal percent was obtained at initial concentration of 20 mg/L and hence, this point was selected as optimum initial concentration of dye. Because of fast adsorption of MO molecules on ZnS/CNTs nanocomposite surface by increasing of dye concentration, high number of hydroxyl radicals are needed for degradation of methyl orange, but for a given irradiation time and ZnS dosage, the number of produced hydroxyl radicals are constant and hence, removal efficiency was decreased.

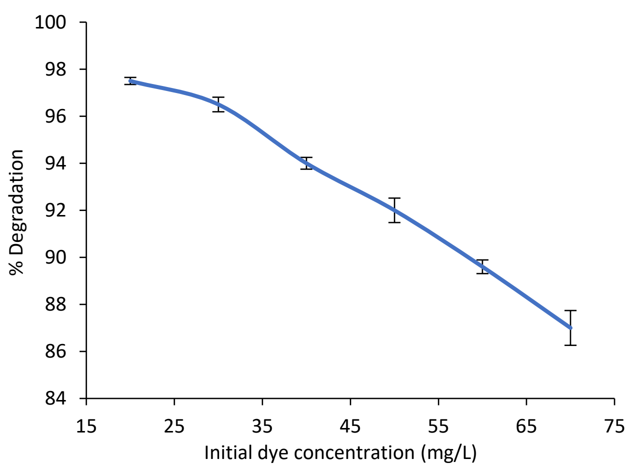

Fig. 3. Effect of initial concentration of dye on degradation efficiency. (Experimental conditions: amount of ZnS/CNTs: 0.3 gr, pH: 2, contact time: 2 mi

3.4. Effect of time on degradation efficiency

For evaluation of effect of time on removal efficiency of methyl orange, several reaction times between 0.5 to 3 minutes were examined. Results showed that best removal efficiency of MO was obtained at 2.5 minutes after beginning of experiment and this time was selected for further experiments (Figure 4).

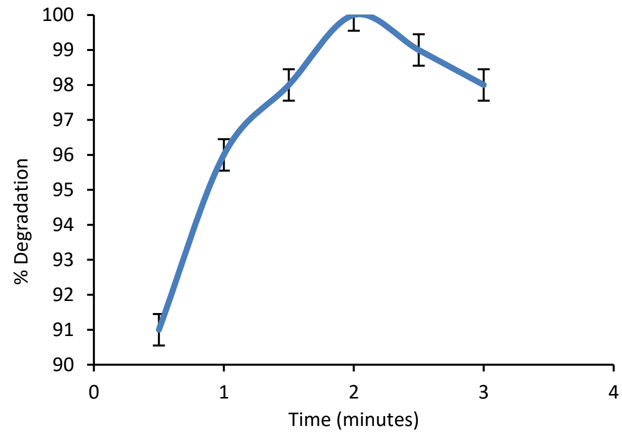

Fig. 4. Effect of time on degradation efficiency (Experimental conditions: amount of ZnS/CNTs: 0.3 gr, initial dye concentration: 20 mg/L, pH: 2)

3.5. Effect of inorganic species on degradation efficiency

Real wastewater often contains organic and inorganic ions that affected activity of nanocatalyst. For studying effect of other species on degradation efficiency of MO, several ions such as chloride, carbonate, and sulfate were added to dye solution. All experiments were performed using 20 mg/L of MO and 0.3 gr/L of nanocatalyst. Concentrations of inorganic species were 20 mg/L Figure 5 showed that in presence of inorganic ions, degradation efficiency of MO was decreased.

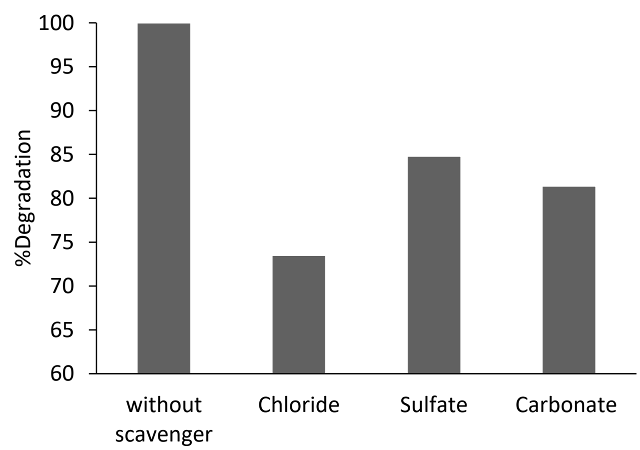

Fig. 5 Effect of inorganic species on degradation efficiency

Chloride anions has highest decreasing effects on removal efficiency due to the it's scavenging effect. Following reactions expressed scavenging effects of chloride, carbonate and sulfate anions, respectively:

$$Cl^- + OH^o \rightarrow Cl^o + OH^- \quad (3)$$

$$SO_4^{2-} + OH^{o} \rightarrow SO_4^{o} + OH^{-} \quad (4)$$

$$CO_3^{2-} + OH^{o} \rightarrow CO_3^{o} + OH \quad (5)$$

3.6. Comparison of different method for degradation of MO

A comparative study of different method for degradation of methyl orange are depicted in fig. 6. The values of initial dye concentration, CNT/ZnS dosage and pH were constant at 20 mg/L, 0.3 g/L and 2. As shown in Figure 6 sonocatalytic removal efficiency in the presence of CNT/ZnS catalyst is higher than that of ZnS and CNT under similar conditions. In addition, the degradation efficiency of methyl orange in the presence of US/ZnS/CNT and US/ZnS is higher than that of ZnS/CNT and ZnS indicating the important role of ultrasound irradiation for production of active radical from ZnS/CNT nanocatalyst [19]. Comparison of ZnS/ CNT and ZnS for the adsorption of methyl orange showed that increasing in surface area of nanocatalyst, enhance production of hydroxyl radicals as oxidizing agent [20]. Briefly, ultrasound can enhance mass transfer diffusion and increased production of hydroxyl radicals [20]. karaca et al., [21] reported similar results for sonocatalytic degradation of naproxen catalyzed by zinc oxide nanoparticles on montmorillonite particles under ultrasonic irradiation in aqueous solution. Table 1 showed a comparison of proposed technique with those previously reported studies for removal of MO dye from aqueous solutions. As shown in Table 1 fast equilibrium time, high adsorption capacity, high removal efficiency and other advantages are obtained for removal of methyl orange.

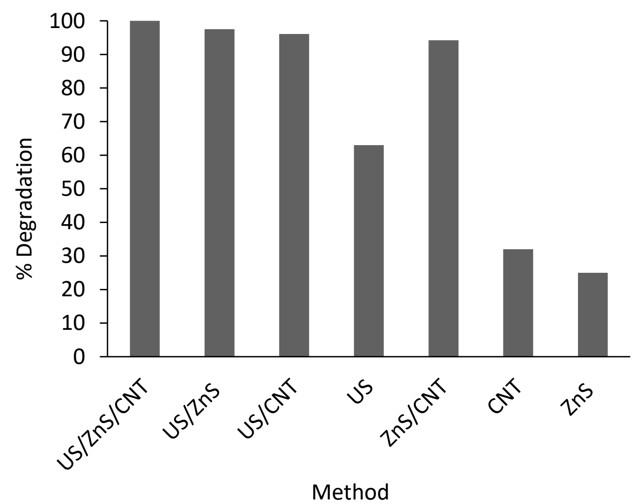

Fig. 6 Comparison of different method for degradation of MO

Table. 1 Comparison of proposed method with other reported technique for removal of MO

Method	Adsorption Capacity(mg/g)	Contact time(min)	References
Fe_2O_3/SiO_2/CS composite	34.29	60	[22]
Carbon coated monolith	23-47	1440	[23]
Tamarisk-activated carbon	3.84	45	[24]
Mesoporous Fe_3O_4–SiO_2–TiO_2	2.5	48	[25]
MWCNTs	53	3.4	[26]
MWCNTs/ZnS	62	2.5	This study

3.7. Reusability and adsorption capacity of nanocatalyst

Nanocatalyst reusability is a very important factor from an economical point of view. For this purpose, experiments were performed at optimized condition. After that, the nanocatalyst was washed, dried and reused for next run. Results showed that degradation efficiency was decreased from 100 to 97.4 after 4 repeated experiments that confirmed reusability of nanocatalyst. Also, for evaluation the sorption capacity of nanocatalyst a standard solution containing 2000 mg/L of MO was applied. The initial and final amounts of MO were determined by spectrophotometer. The maximum adsorption capacity was defined as the total amount of adsorbed MO per gram of the catalyst. The obtained capacity was found to be 62 mg/g.

4. Conclusions

In this study ZnS/CNT nanocatalyst was synthesized and applied for sonocatalystic removal of methyl orange. Best degradation efficiency obtained at pH, 2, while 0.3 gr of nanocatalyst was used. Also, in comparison of several methods for degradation of MO results showed that complete degradation of methyl orange was obtained in presence of ultra sound that confirmed role of nanocatalyst for production of hydroxyl radicals. Also, reusability of nanocatalyst was suitable for real application in wastewater.

Acknowledgements

Authors hereby thanks from health laboratory of Zabol University for cooperation to perform experiments.

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