

Photodegradation of HMX and RDX in the Presence of Nanocatalyst of Zinc Sulfide Doped with Copper

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ABSTRACT: *Nanoparticles of zinc sulfide as undoped and doped with copper were used as photocatalyst in the photodegradation of HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) as nitramine explosives under UV and Vis irradiations. Photoreactivity of doped zinc sulfide was varied with dopant, mole fraction of dopant to zinc ion, pH of solution, dosage of photocatalyst and concentration of explosive. The characterization of nanoparticles was studied using XRD patterns, UV-Vis spectra and TEM image. The maximum degradation efficiency was obtained in the presence of $Zn_{0.95}Cu_{0.05}S$ as nanophotocatalyst. The effect of dosage of photocatalyst was studied in the range of 50-200 mg/L. It was seen that 150.0 mg/L of photocatalyst is an optimum value for the dosage of photocatalyst. The most degradation efficiency was obtained in neutral pH of 7.0 with study of photodegradation in pH amplitude of 2-12. In the best conditions, the degradation efficiency of HMX and RDX was obtained 92-94 %. A gradual decrease in the degradation efficiency was observed at the first two cycles.*

KEY WORDS: *Photodegradation, Photocatalyst, Zinc sulfide, RDX, HMX, Nanoparticles.*

INTRODUCTION

Among the various explosives, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are two main explosive substances used by munitions industries [1, 2]. However, these substances are carcinogenic and, therefore, the corresponding wastes present both environmental and health concerns [3-6]. Additionally these substances are normally difficult to degrade. Therefore, the soils and groundwater near the munitions factories are seriously contaminated.

Among various physical, chemical and biological techniques for treatment of wastewaters, heterogeneous

photocatalysis has been considered as a cost-effective alternative for water remediation [7, 8]. The superiority of photocatalytic technique in wastewater treatment is due to its advantages over the traditional techniques, such as quick oxidation, no formation of polycyclic products, oxidation of pollutants in the ppb range [9, 10].

Nano-scale semiconductor particles possess higher surface area-to-volume ratio than their bulk counterparts, and thus allow for greater photon absorption on the photocatalyst surface. Moreover, recombination of the electron-hole pair within the semiconductor particle is drastically reduced as particle size decreases.

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With decreasing the particle size of semiconductor to nanometer-size scale, the band-gap energy increased greatly, which in turn led to higher redox potentials in the system. Therefore, the nano-scale semiconductor is expected to have higher photocatalytic activity than its bulk [11-13].

This paper reports the use of nanoparticles of zinc sulfide as undoped and doped with Cu as photocatalyst in degradation of RDX and HMX as nitramine explosives under ultraviolet (UV) and visible (Vis) irradiations. The nanoparticles were prepared using a simple route via co-precipitation method in the presence mercaptoethanol as capping agent. The influence of parameters are studied for achieve to degradation efficiency of explosives near 100%.

EXPERIMENTAL

Materials

HMX and RDX of the highest purity available (greater than 99 % as judged by high-performance liquid chromatography [HPLC]), were kindly provided by the defense research group of Malek-ashtar University of Technology. For preparation of simulated HMX and RDX wastewaters 4.0 and 40.0 mg of HMX and RDX, respectively, was dissolved in 10 mL of acetone and the solution was then added slowly to a 1000 mL beaker containing 800 mL of water (80 °C). Beaker was heated up continuously until no acetone could be detected and the process lasted for ca. 4h. After cooling at room temperature, the solution was transferred to a brown capacity bottle of 1000 mL, and diluted with water to the graduation mark. The prepared solutions with concentration of 4.0 and 40.0 mg/L were the simulated HMX and RDX, respectively, wastewaters and stored at room temperature for later use.

The chloride salts of zinc (ZnCl_2) and copper ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), all from Merck, were used as source of metal ions and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (Merck) was used as source of sulfide ion. 2-Mercaptoethanol (2-hydroxyethanethiol, $\text{HOCH}_2\text{CH}_2\text{SH}$) and isopropyle alcohol were prepared from Merck Company and used as received. Hydrochloric acid and sodium hydroxide were applied for variation of pH of sample solutions. Methanol and acetonitrile were chromatographic grade from Merck Company. Double-distilled water used for preparation of solutions and tap-water (Ca^{2+} ; 3.5 mg/L, Mg^{2+} ; 2.2 mg/L

and Na^+ ; 2.5 mg/L) was used for preparation of the simulated HMX and RDX wastewater.

Catalyst preparation

The nanoparticles of $\text{Zn}_{1-x}\text{S}:\text{Cu}_x$ ($x=0, 0.02, 0.05$ and 0.10) were synthesized using controlled precipitation and co-precipitation methods. Initial, 50 mL homogeneous solutions 0.01 M of ZnCl_2 and CuCl_2 as mole ratio of $[\text{Cu}^{2+}]/[\text{Zn}^{2+}] = x$ and 50 mL solution of 0.1 M mercaptoethanol were added in a balloon (three-vent) on a magnetic stirrer. Then, 50 mL solution of 0.01 M sodium sulfide was added drop by drop using a decanter vessel (each 6-8 s, one drop) under nitrogen atmosphere while the mixture was stirred vigorously at room temperature. The precipitated nanoparticles of $\text{Zn}_{1-x}\text{Cu}_x\text{S}$ were then centrifuged at 4000 rpm, washed three times with water to eliminated unreacted ions, and finally washed three times with isopropyl alcohol. The cleaned powders were dried for about 10 h at 80 °C until complete evaporation of the solvent was achieved. To this way, the nanoparticles of ZnS and ZnS:Cu with percentages of 2, 5 and 10% of doped ion were purchased.

Apparatus

A Siemens D-5005 diffractometer using Cu K_α irradiation ($\lambda=1.5418 \text{ \AA}$) was used for X-ray powder diffraction (XRD) patterns of nanoparticles. Transmission electron micrographs (TEMs) of the nanoparticles were taken by a JEOL JEM-1200EXII electron microscope operating at 120 kV. The pH value of the solutions was determined by a Metrohm 661 pH meter.

Chromatographic system of Agilent Technologies (HP) consisting of a quaternary pump with micro vacuum degasser, a 20 μL injector (Agilent 1200 series manual injector), a 1200 series ultraviolet variable wavelength detector and a temperature controlling module for HPLC-UV analysis was used. Typically, 2 and 20 μL of the RDX and HMX, respectively, containing wastewater were directly injected into a Microsorb-MV 100 C18 column (25 cm \times 4.6 mm, 5 μm). The mobile phase of the column was a mixture of methanol and water with volume ratio of 50:50 and the flow-rate was 1 mL/min. The column temperature was maintained at 30 °C and the running time was 20 min. An ultraviolet detector set at 254 nm was used. The analyzing of chromatograms was done using HPLC 2D chemstation software.

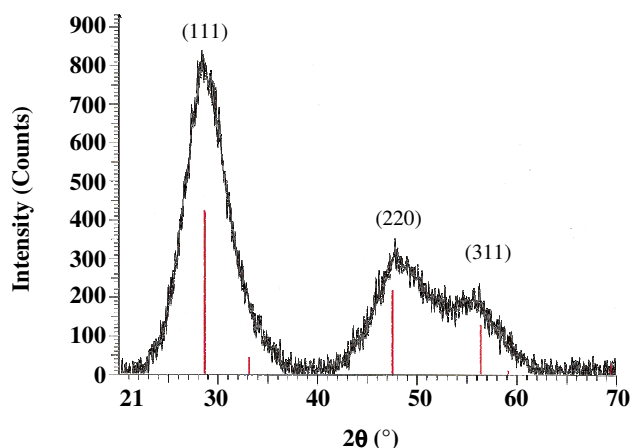


Fig. 1: X-ray diffraction patterns of ZnS:Cu (5 %) nanocrystals.

Photodegradation experiments

Photodegradation experiments were performed with a photocatalytic reactor system. This bench-scale system consisted of a cylindrical Pyrex-glass cell with 1.0 L capacity, 10 cm inside diameter and 15 cm height. A 100 W mercury lamp as the UV light source and/or a 500-W halogen lamp as the Vis light source were placed in a 5 cm diameter quartz and/or glass tube, respectively, with one end tightly sealed by a Teflon stopper. A cutoff filter was applied to remove wavelengths below 420 nm to ensure irradiation completely by visible light. 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 0.5 L of 4.0 and 40.0 mg/L of HMX and RDX, respectively, as pollutant and 50.0-200.0 mg/L of nanoparticles as nanophotocatalyst. The whole reactor was cooled with a water-cooled jacket on its outside and the temperature was kept at 25 °C. All reactants in the reactions were stirred using a magnetic stirrer to ensure that the suspension of the catalyst was uniform during the course of the reaction. To determine the percent of destruction of nitramine explosives, the samples were collected at regular intervals, filtered through Millipore membrane filters, and centrifuged to remove the nanocatalyst particles that exist as undissolved particles in the samples.

Degradation efficiency (% D) of explosives was determined using chromatogram peak area of RDX and/or HMX before and after degradation in selected time intervals with using HPLC. The degradation efficiency has been calculated as:

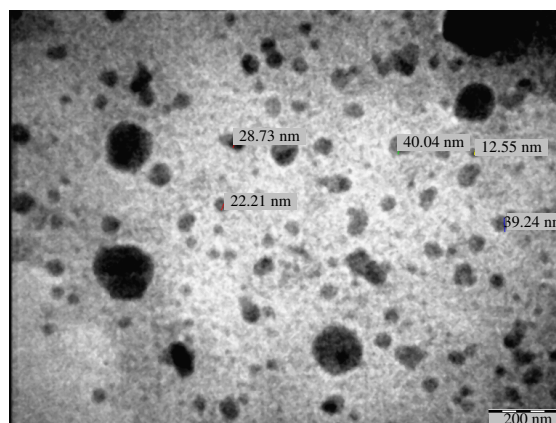


Fig. 2: TEM image of nanoparticles of ZnS:Cu (5 %).

$$\% D = 100 \times [(S_0 - S)/S_0]$$

Where S_0 and S is the peak area of explosive before and after degradation in selected time intervals, respectively.

In order to obtain maximum degradation efficiency of HMX and RDX, the influence of variables such as pH of solutions, concentrations of explosives and amount of photocatalyst were studied. The experiments were carried out in the presence of nanoparticles of ZnS and ZnS:Cu with percentages of 2, 5 and 10 % of doped ion.

RESULTS AND DISCUSSION

Characterization of nanoparticles

The XRD pattern of ZnS doped with 5 % Cu as a sample is shown in Fig. 1. It reveals that the particles exhibit a zinc-blend crystal structure. The three diffraction peaks correspond to (111), (220) and (311) planes of the cubic crystalline ZnS [14, 15]. Also, transmission electron micrographs (TEM) images confirmed the formation of ZnS:Cu(5%) nanoparticles with diameters of 10-40 nm (Fig. 2).

Photodegradation of HMX and RDX using nanophotocatalysts

In Fig. 3, comparison of photodegradation of HMX and RDX explosives with initial concentration of 4.0 and 40.0 mg/L, respectively, is shown in the absence, macrocrystalline and nanocrystalline of ZnS with dosage 100.0 mg/L in time intervals 30 min under UV irradiation. The order photodegradation efficiency for both explosives

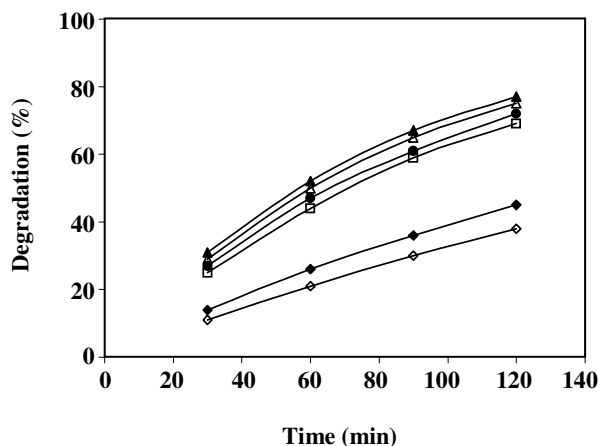


Fig. 3: Photodegradation of HMX (full marker) and RDX (empty marker) with initial concentration of 4.0 and 40.0 mg/L, respectively, in the absence (\diamond), macrocrystalline (\bullet) and nanocrystalline (\blacktriangle) of ZnS with dosage 100.0 mg/L.

is obtained: without ZnS < macrocrystalline ZnS < nanocrystalline ZnS. ZnS is a semiconductor and photodegradation of an organic pollutant is initiated by the photoexcitation of the semiconductor. The electron / hole pair is obtained from photoexcitation of ZnS and the high oxidative potential of holes can be lead to direct and indirect oxidation of explosives. In the indirect oxidation process of explosives, the hydroxide reactive radicals ($\bullet\text{OH}$) were formed from combination of holes with water molecules and/or hydroxide anions. The radical hydroxide with $E^\circ = +3.06$ V is a strong oxidative and oxidize explosives as non-selective to mineral species as partial or complete [16, 17].



In photocatalysis process, the total number of free carriers (electron/hole) on the surface of photocatalyst determines the efficiency of catalyst. For large particles, the volume recombination of electrons and holes dominates. This condition largely reduces the number of free charges on the surface and deteriorates the photocatalytic activity. For nanoparticles, the transportation length of electron/hole from crystal interface to the surface is short, which helps to accelerate the migration rate of electron/hole to the surface of the nanoparticle to participate the reaction process. This pointer and

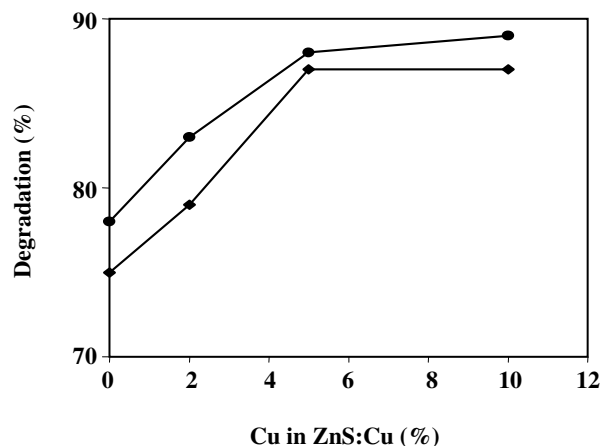


Fig. 4: Photodegradation of HMX (\bullet) and RDX (\blacklozenge) with initial concentration of 4.0 and 40.0 mg/L in the presence of nanoparticles of ZnS doped with Cu dosage 100.0 mg/L in irradiation time of 120 min.

increasing of accessible surface of photocatalysts as nanoparticles lead to increasing of photodegradation rate of explosives [18, 19].

As mentioned, the number and the lifetime of free carriers (electrons/holes) are particle size- and dopant-dependent. In order to investigation of effect of dopant, the photodegradation efficiency of explosives was studied in the presence of ZnS:Cu (2, 5 and 10 %) nanoparticles (100.0 mg/L) in irradiation time of 120 min. The obtained results are given in Fig. 4. As seen, the maximum photodegradation efficiency was obtained in the presence of ZnS:Cu(5 %). Increasing of mole fraction of Cu^{2+} and use of $\text{Zn}_{0.90}\text{Cu}_{0.10}\text{S}$ as photocatalyst did not lead to more increasing of degradation efficiency. On the other hand, the most degradation for both explosives was occurred using $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{S}$ as photocatalyst in among of prepared nanoparticles. Doping of ZnS with other transition metal ions offers a way to trap charge carriers and extend the lifetime of one or both of the charge carriers. Consequently, dopants enhance the efficiency of the photocatalyst [20].

The Cu^{2+} ion with $E^\circ = +0.337$ V can be act as an oxidizing agent. In the other word, the Cu^{2+} ion can be reduced to Cu^+ ion by a hole produced with semiconductor. The resulting ion (Cu^+) is a strong oxidative ($E^\circ = +0.521$ V) and hence it also can be an oxidizing agent for organic pollutants. As a result, in these conditions, in beside of holes and hydroxyl radicals, Cu^{2+} and Cu^+ ions, also, act as oxidizing agents and therefore, the rate of degradation was increased.

Table 1: Apparent degradation rate constant (*k*) and standard deviation (*n*=3) of HMX and RDX with initial concentrations of 4.0 and 40.0 mg/L, respectively.

Photocatalyst	HMX	RDX
Without photocatalyst	$5.0 \pm 0.3 \times 10^{-3} \text{ min}^{-1}$	$4.0 \pm 0.2 \times 10^{-3} \text{ min}^{-1}$
ZnS macrocrystalline	$10.5 \pm 0.2 \times 10^{-3} \text{ min}^{-1}$	$9.8 \pm 0.3 \times 10^{-3} \text{ min}^{-1}$
ZnS nanocrystalline	$12.4 \pm 0.2 \times 10^{-3} \text{ min}^{-1}$	$10.6 \pm 0.3 \times 10^{-3} \text{ min}^{-1}$
Zn _{0.98} Cu _{0.02} S	$15.0 \pm 0.4 \times 10^{-3} \text{ min}^{-1}$	$13.2 \pm 0.4 \times 10^{-3} \text{ min}^{-1}$
Zn _{0.95} Cu _{0.05} S	$18.0 \pm 0.3 \times 10^{-3} \text{ min}^{-1}$	$16.8 \pm 0.4 \times 10^{-3} \text{ min}^{-1}$
Zn _{0.90} Cu _{0.10} S	$18.1 \pm 0.4 \times 10^{-3} \text{ min}^{-1}$	$16.7 \pm 0.3 \times 10^{-3} \text{ min}^{-1}$

Many authors have reported that the kinetic behavior of photocatalytic reaction can be described by a modified Langmuir-Hinshelwood model [21, 22].

$$1/r_0 = 1/k + 1/kKC_0$$

In the above equation r_0 , k , K and C_0 are initial rate, rate constant, equilibrium absorption constant and initial concentration of pollutant, respectively. At high substrate concentration, adsorbed reactant molecules may occupy all the catalytic sites on the catalyst surface and this leads to zero-order kinetics. At low concentration, the number of catalytic sites will not be limiting factor and the rate of degradation is proportional to the substrate concentration, in accordance with apparent first-order kinetics. In order to confirm the speculation, $\ln(C_0/C)$ was plotted as a function of the irradiation time. The calculated results indicated that the first-order model gives a better fit. The apparent degradation rate constant (k) of explosives with initial concentrations of 4.0 and 40.0 mg/L of HMX and RDX, respectively, were calculated and collected in table 1.

Effect of variables influence on degradation efficiency

The initial rate of photocatalytic degradation of many pollutants is a function of the photocatalyst dosage [23, 24]. Fig. 5 illustrates photodegradation of HMX and RDX in the dosage 50.0-200.0 mg/L of nanocatalysts Zn_{0.95}Cu_{0.05}S with irradiation time of 120 min. Because increasing in active sites, the rate degradation is increased to maximum degradation efficiency in the presence amount of 150.0 mg/L of nanophotocatalyst. However, as the loading was increased beyond the optimum amount, the degradation rate decreased due to increasing the opacity of the suspension samples and therefore increasing the light scattering. In these conditions, the

penetration depth of the photons is decreased and less catalysts nanoparticles could be activated.

Photodegradation of HMX and RDX, 4.0 and 40.0 mg/L, respectively, was studied in amplitude pH of 2.0-12.0 in the presence of nanocatalyst Zn_{0.95}Cu_{0.05}S (150.0 mg/L). The results for irradiation time of 120 min are shown in Fig. 6. The maximum degradation efficiency was obtained in neutral pH 7 for both explosives. In the presence of Zn_{0.95}Cu_{0.05}S and in pH 7, degradation efficiency 91.0 and 93.0 % for RDX and HMX is obtained, respectively.

The zeta (ζ) potential data for nanocatalyst of Zn_{0.95}Cu_{0.05}S is shown in Fig. 7. The results show isoelectric points (IEP) in amplitude pH of 7.0-7.5. Therefore, the surfaces of photocatalyst are positively charged in acidic solutions and negatively charged in alkaline solutions [25]. A low pH is associated with a positively charged surface which cannot provide hydroxyl group which are needed for hydroxyl radical formation. As the other words, at low pH, the adsorption of cationic organic pollutants on the surface of photocatalysts decreased because the photocatalysts surface will be positively charged and repulsive forces is due to decreasing adsorption. Thus, the degradation efficiency will be decreased in acidic pH.

On the other hand, higher pH value can provide higher concentration of hydroxyl ions to react with the holes to form hydroxyl radicals. Apparently, in pH 7, because neutrality charge surface of catalyst, the most adsorption of molecules of RDX and/or HMX was occurred and the maximum degradation were obtained. But, the degradation of explosives was inhibited when the pH value is more than 7 because the hydroxyl ions compete with explosives molecules in adsorption on the surface of photocatalysts [26].

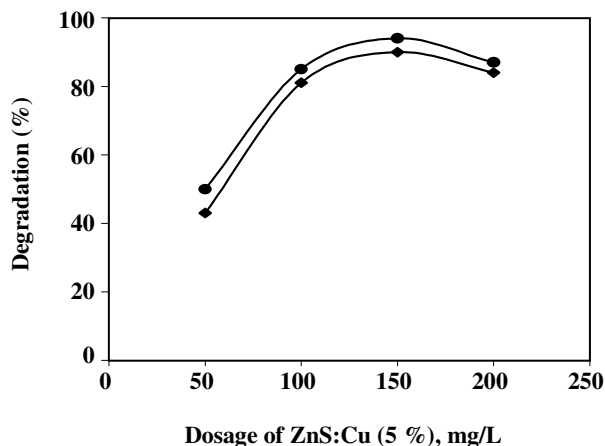


Fig. 5: Effect of dosage of ZnS:Cu (5 %) on the photodegradation of HMX(●) and RDX (◆).

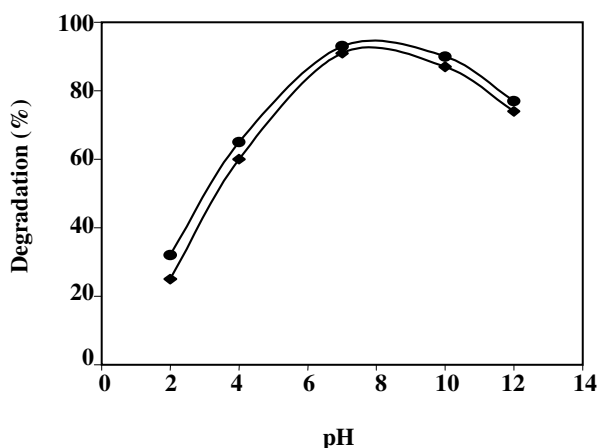


Fig. 6: Effect of pH of solution on the photodegradation of HMX(●) and RDX (◆).

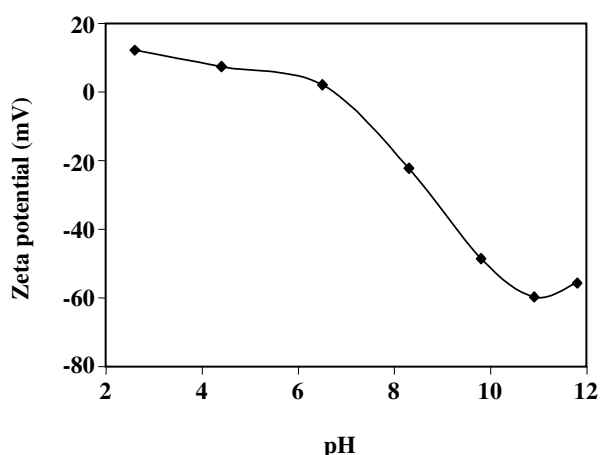


Fig. 7: Zeta potential of Zn_{0.95}Cu_{0.05}S nanocatalyst as a function of pH value.

The degradation efficiency of explosives with various initial concentrations of 1, 2, 3 and mg/mL and 10, 20, 30 and 40 mg/mL of HMX and RDX, respectively, were investigated. In both case, the rate of degradation and therefore the degradation efficiency were increased with increasing of the explosive concentrations. Therefore, degradation efficiency is independent of the initial concentrations of HMX and RDX in the wastewater samples [27].

Reproducibility of the nanocatalyst ZnS:Cu (5 %)

The reproducibility of Zn_{0.95}Cu_{0.05}S as nanocatalysts was studied for HMX and RDX photodegradation during a three cycles experiment. Each experiment was carried out under identical conditions of 4.0 and 40.0 mg/L of HMX and RDX, respectively, 150.0 mg/L of nanocatalyst, pH of 7, irradiation time of 120 min and at room temperature. After each degradation experiment, the concentration of explosives was adjusted back to its initial values. A gradual decrease in the activity of nanocatalysts was observed at the first two cycles with degradation of 93.5 and 88% for HMX and 91.5 and 85.3 % for RDX. But, decreasing of the activity was seen intense after the first and second cycles.

Photodegradation of HMX and RDX under visible irradiation

In order to comparison photodegradation efficiency of HMX and RDX under UV and Vis irradiations, degradation of explosives with using Vis light was studied under optimum conditions of UV light. Degradation efficiency of HMX and RDX under Vis irradiation is obtained 81.5 and 78.2 %, respectively, in time duration of 120 min., whereas destruction of 93.2 and 91.0 % for HMX and RDX, respectively, is resulted under UV irradiation. This result is not unexpected because the energy of visible radiation is less than energy of ultraviolet radiation.

CONCLUSIONS

Semiconductor of zinc sulfide as undoped and doped with copper can be used as a photocatalyst in the process of photodegradation of nitramine explosives such as HMX and RDX. In the presence of nanophotocatalysts, the degradation efficiency is increased due to increase of applicable surface of photocatalyst as well as accelerate

migration rate of electron/hole to the surface of the nanoparticles. The kinetics of the photodegradation in the presence of the nanocatalysts follows a first-order rate model.

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