

Use of Sonication Advanced Oxidation Processes for Purification of Energetic Wastewater

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Abstract: The production and use of nitro-aromatic explosives for military operations have resulted in environmental pollution, their presence in waterways has an ecological and health hazard. Energetic water generate large amount of aromatic compounds and aliphatic nitro-amines. Development of Advanced oxidation processes (AOPs) is of great importance in order to remove these compounds. AOPs occupy an important place in environmental-protection technologies. They are effectively used in water purification from harmful substances to human health and the environment. The study was performed for pretreated samples with ozone or potassium ferrate-VI as oxidants and cationic polyelectrolyte (Zetag-92) or liquid bittarn as coagulants. Using only sonolysis (US) or photocatalysis (UV) any or poor degradation showed Total organic carbon (TOC) and Chemical Oxygen demand (COD) value. However combination of both processes (US + UV) increases pollutants reduction. TiO_2 photocatalyst was utilized in the presence of air and UV radiation ($\text{nm} > 380$) approximately. In this study the coagulation pretreatment using cationic polyelectrolyte (zetag-92) followed by sonophotocatalysis showed TOC removal 94.35%. While liquid bittarn as coagulant showed TOC removal 85.32%. Using ozone pretreatment effect followed by sonophotocatalysis achieved TOC and COD removal 84.55% and 93.83% respectively. The potassium ferrate-VI oxidation and sonophotocatalysis succesively showed the least demineralization of pollutants in energetic wastewater. The photo-catalytic degradation of energetic nitro-amines effluents on exposure to UV light, using titanium-dioxide slurry as catalyst in combination with ultra sonic waves was held after performing the four types of pretreatment. The results are illustrated and confirmed by high performance liquid chromatography (HPLC) analysis. Ozone pretreatment in combination with sonophotocatalysis showed the best tool for demineralization of pollutants in wastewater effluent.

Key words: Nitro-aromatic compounds • Treatment • UV • catalyst • TiO_2 • ozonation

INTRODUCTION

In the natural environment refractory pollutants are only partly biodegradable and, therefore, they are not easily removed in biological wastewater treatment plants [1]. Nitro-aromatic explosives are toxic and their environmental transformation products, including arylamines, arylhydroxylamines and condensed products such as azoxy-and azo-compounds, are equally or more toxic as the parent nitro compounds are resistant to chemical or biological oxidation and to hydrolysis because of the electron-withdrawing nitro groups [2]. That is why there is a need to develop effective method for the degradation of these pollutants, either to less harmful compounds or to their complete mineralization. A wide range of organic compounds is detected in industrial

and municipal wastewater. Some of these compounds (both synthetic organic chemicals and naturally occurring substances) pose severe problems in biological treatment system due to their resistance to biodegradation or/and toxic effects on microbial processes.

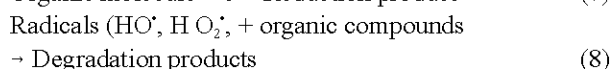
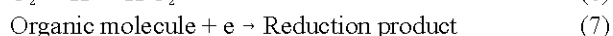
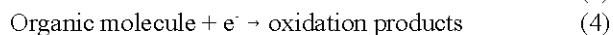
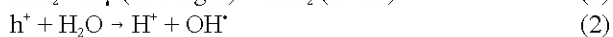
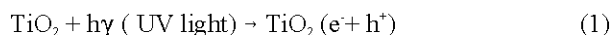
As a result, the use of alternative treatment technologies, aiming to mineralize or transform refractory molecules into others which could be further biodegraded, is a matter of great concern. Among them, advanced oxidation processes (AOPs) have already been used for the treatment of wastewater containing recalcitrant organic compounds such as pesticides, surfactants, coloring matters, pharmaceuticals and endocrine disrupting chemicals.

Moreover, they have been successfully used as pretreatment methods. In order to reduce the

concentrations of toxic organic compounds that inhibit biological wastewater treatment processes [3]. Advanced oxidation processes (AOPs), which involve the generation of highly potent chemical oxidants such as the hydroxyl radical ($^{\bullet}\text{OH}$), have recently emerged as an important class of technologies for accelerating the oxidation and destruction of wide range of organic contaminants in polluted water [4]. Advanced oxidation process (AOPs) employ reactive oxidizing agents such as hydrogen peroxide or ozone, with or without the addition of catalysts or photolysis. Many (AOPs) technologies generate hydroxyl radicals [a strong oxidant, $E^{\circ} = -2.8\text{V}$], addition of which to aromatic rings initiates ring opening and ultimate mineralization to CO_2 and H_2O [5].

Photocatalysis is an active subject for research in environmental protection while development and application of sonolysis (ultrasound) is starting to gain an important place in this domain. In the common problem associated is the reduced efficiency of photo-catalyst with continuous operation possibly due to the adsorption of contaminants at the surface and blocking of the UV activated sites, which makes them unavailable for the destruction. Thus, our aim should be in devising a technique for proper continuous cleaning of the catalyst surface during the photocatalytic operation [6]. Ultrasonic process is selected as a treatment method owing to its several advantages inducing decomposition of volatile and semi-volatile organic compounds in aqueous phase and transformation of the refractory compounds into highly degradable products [7]. Ultrasonic irradiation is one such technique that can be used simultaneously with UV irradiation. Suggesting that two techniques will give better results when operated in combination is the fact that for both techniques (US and UV) basic reaction mechanism is the generation of free radicals and subsequent attack by these on the pollutant organic species. Hence, when the two modes of irradiation are operated in combination, more free radicals will be available for the reaction attack by the hydroxyl radical [8]. Sonolysis, photocatalysis and ozonation are advanced oxidation techniques, which can efficiently be applied also in combination, are able to achieve the complete destruction (i.e. demineralization to carbon dioxide and HCl) of organic chemicals, without the undue formation of secondary pollutant [9-11]. The rate of sonochemical decomposition is directly linked to the OH^{\bullet} availability in the solution. The degradation is more efficient for the higher frequency because the rates of OH^{\bullet} formation in water saturated with air are more at higher frequency [12]. In heterogeneous photolysis, near-UV

photons excites electrons into the conduction band of a semiconductor (usually TiO_2). In order to achieve high photoactivity for titanium particles, it is important to calcine titanium particles at high temperature, preferably without forming rutile phase. The increase of preparation temperature makes titanium particles turn into higher crystalline and leads the increase of photoactivity. This high crystallinity reduce the bulk recombination of photo-excited electron/hole pairs. Consequently, the effective separation of the photoexcited electron/hole pairs could be possible and help the diffusion of them out to the surface of titanium. So, the surface density of electron and hole could be increased. As a result, the photoactivity is enhanced [13]. The resulting "positive holes" oxidize water to hydroxyl radicals which oxidize the substrate at the semiconductor or surface or free in solution. In the presence of oxygen the promoted electrons yield superoxide radical anions, which may themselves attack nitro-aromatic explosives [14]. The following reactions represent the mechanism of the oxidation and reduction sequence:



Organic compounds can undergo oxidative degradation through their reactions with valence bond holes, hydroxyl and peroxide radicals as well as reductive cleavage through their reactions with electrons. So far, TiO_2 /UV light process has been extensively used for wastewater treatment. The keys advantages of this process are the operation at ambient conditions, the lack of mass transfer limitations when nanoparticles are used as photocatalysts and the possible use of solar irradiation. Moreover, TiO_2 is a cheap, readily available material and the photogenerated holes are highly oxidizing. In addition, TiO_2 is capable for oxidation of a wide range of organic compounds into harmless compounds such as CO_2 and H_2O [15].

Potassium ferrate (K_2FeO_4) is a powerful oxidant in the entire pH range and can be used as an oxidant in natural waters. Its potential (E° , $V = 2.20$) $\text{Fe}_4^{2-} + 8\text{H}^+ + 3e^- \rightarrow \text{Fe}^{3+} + 4\text{H}_2\text{O}$.

It is a black-purple compound that remains stable in moisture excluded air for a long period of time. In aqueous solution, the ion FeO_3^- is monomeric with a high degree of four "covalent character" equivalent oxygen atom. The reduction of Fe (VI) results in a relatively non-toxic by-product iron (III), which suggests that potassium ferrate (VI) in conjunction with an appropriate heterogeneous catalyst in non-aqueous media can efficiently oxidize a number of organic compounds [16]. Potassium ferrate (VI) has shown great promise as a multi-purpose wastewater treatment chemical for coagulation disinfection and oxidation. Fe (VI) removes more turbidity from the model colloidal system than Fe (III) and Fe (II) salts. Fe (VI) is very effective in inactivating indicator organisms and known pathogens in the *Enterobacteriaceae* family at concentrations of 5×10^{-5} M. The ability of Fe(VI) to inactivate viruses has also been studied [17].

The aim of this study is to test different AOPs processes singly and combined with, sonication, UV-light and TiO_2 as local material for energetic wastewater degradation. Four types of pretreatment, ozone and potassium ferrate-VI as oxidants and zetage-92 or liquid bittern as coagulants were tested before subjecting to combination with sonophoto treatment. The combination was held to test the complete demineralization of energetic wastewater. Characteristics of this wastewater were illustrated in Table 1.

MATERIALS AND METHODS

2.1. Raw Materials: Energetic wastewater samples used for experimental purpose were collected from end pipe effluent. Table 1 illustrated the characteristics of this effluent.

Cationic Flocculants: An imported polyelectrolyte (Zetag 92), which acts as cationic polyelectrolyte was used at a dose of 10 mg/L for coagulation pre-treatment of energetic wastewater.

Inorganic coagulant, liquid bittern (LB) was obtained from Egyptian Salts and Minerals CO. The characteristics of bittern are listed in Table 2. A dose of 0.294 g/L of Mg^{++} ion was used.

Ozone gas was generated using a Sol-Fischer ozone generator. The dose used was 0.5 mg/L was bubbled into 1000 ml wastewater for 6 minutes.

Potassium Ferrate (IV) was used as coagulant and oxidant with a dose of 30 mg/L for pretreatment. It was prepared by electro-chemical method. Cast iron was used

Table 1: Characteristics of Energetic wastewater

Parameters	Value	Limits in law 48 to the year 92
pH	2.74	6-9
Color	Brown with suspension	Colorless
COD mgL^{-1}	948	20-100 mgL^{-1}
TDS mgL^{-1}	1022	800-2000 mgL^{-1}
TS mgL^{-1}	1546	1000 mgL^{-1}
TSS mgL^{-1}	456	30-60 mgL^{-1}
Total oil grease mgL^{-1}	80	5 mgL^{-1}
Phenols mgL^{-1}	0.48	5 mgL^{-1}
Chlorides mgL^{-1}	124.3	0.001 mgL^{-1}
Iron mgL^{-1}	0.889	1 mgL^{-1}
Mn mgL^{-1}	0.40	1 mgL^{-1}
Electric conductivity ms/cm	1.60	0.5 mgL^{-1}
Mg mgL^{-1}	53.5	--
SO_4 mgL^{-1}	648	--
DOC mgL^{-1}	140	200-400 mgL^{-1}
NO_3 mgL^{-1}	59.83	--
TNT suspension mgL^{-1}	0.68	30 mgL^{-1}
TNT soluble mgL^{-1}	25.86	Nil

Table 2: Typical properties of (LB) Liquid Bittern

Parameter	Value
pH	7.3
conductivity, ms/cm	70
Turbidity, FTU	131
TSS mg/L	120
TDS mg/L	390
Cl^- mg/L	69.65
Ca, mg/L	1200
Mg	45.12
Total alkalinity, as CaCO_3 , mg/L	191.00
Salinity%	2700

as anode and is dissolved and then oxidized to form K_2FeO_4 when a highly concentrated KOH is used as the electrolyte.

TiO_2 Catalyst: TiO_2 (Anatase 80% and 20% rutile) was dried at 600 °C and used in the reaction mixture when UV light was employed [18] stated that at 650 °C the crystallite size growth is insignificant, moreover, the anatase-rutile transformation ratio is negligible and the only crystalline phase observed is anatase.

Standard Jar Test apparatus model [Flocculator SWW. STURA Scientific U.K.] it consists of process multiple stainless steel paddles.

Ultrasonic generator with a titanium horn connected and operated at 500 Khz and with a power output of 120 W.

UV lamp 180 watt (model EM 11 A VP-60) was exposed axially to batch cylindrical glass vessel.

Spectrophotometer (HACH DR-2000) was used for COD and TOC determination.

High Performance Liquid Chromatography (HPLC) model (Waters 486) was used for determination of degradation analyses for pollutants present.

METHODS

Pretreatment steps include coagulation process. In this pretreatment step the calculated dose of the used coagulants, (K_2FeO_4 , $LB\ Mg^{2+}$ and zetag 92) was added to the wastewater then proceeding Jar Test technique as follows: the samples were flash mixed for 5 minutes at high speed. Then the speed of the stirrers was reduced to impart 20 minutes to allow coagulation flocculation to take place. The multiple stirrers were then stopped for 30 minutes quiescent settling period. The supernatants were transferred for photooxidation treatment.

In the oxidation step the wastewater was subjected to ozonation with known dose then the sample proceeded to the following treatment steps.

In Sonophoto-reactions the experiments were performed in a borosilicate cylindrical glass reactor operating in batch mode and covered with aluminum foil in order to provide maximum irradiation of the reaction mixture. UV-irradiation provided by 180 W lamp. A titanium horn connected to an ultrasonic system operating at 500 K Hz and with power output 120W was used as ultrasonic generator. This horn was immersed in water bath containing batch vessel where the active part sonicated is restored to a zone located in the vicinity of the emitter Fig. 1.

Different treatment combinations were evaluated for the pretreated samples. US, US + UV, US + UV + TiO_2 , US + UV + TiO_2 + 10 folds dilution ...up to 15 folds dilution. The TiO_2 catalyst was used as suspension after magnetically stirred for 30 min in dark before the "zero-time" of the experiment to ensure total equilibrium of adsorption/desorption of chemical compounds on the catalyst surface. The "zero-time" for the reaction was established when the UV lamp and / or the ultrasonic generator were turned on. Temperature was maintained between 30-33°C by means of the water bath. Samples were diluted 10-15 folds and air was continuously sparged in the liquid for major radical production. Since in photocatalysis the presence of oxygen is favourable for the reaction of oxygen with the generated conduction band electrons (e^-), which in turn can react with H^+ and generate hydro-peroxide ($HO_2\cdot$) radicals. During sonolysis the air supplied provides additional nuclei for the occurrence of cavitation increasing the amount of free radicals. Samples were periodically withdrawn from the reaction vessel and centrifuged at 4000 rpm in order to separate TiO_2 particles, supernatants were subjected to COD, TOC and HPLC analysis.

Analytical Techniques were performed by (a) Chemical Oxygen Demand (COD) analysis were performed using available solution (HACH) incubated during 120 min at 150°C in COD reactor(Model 45600) and measured colorimetrically in a Hach DR/2000 spectrophotometer.

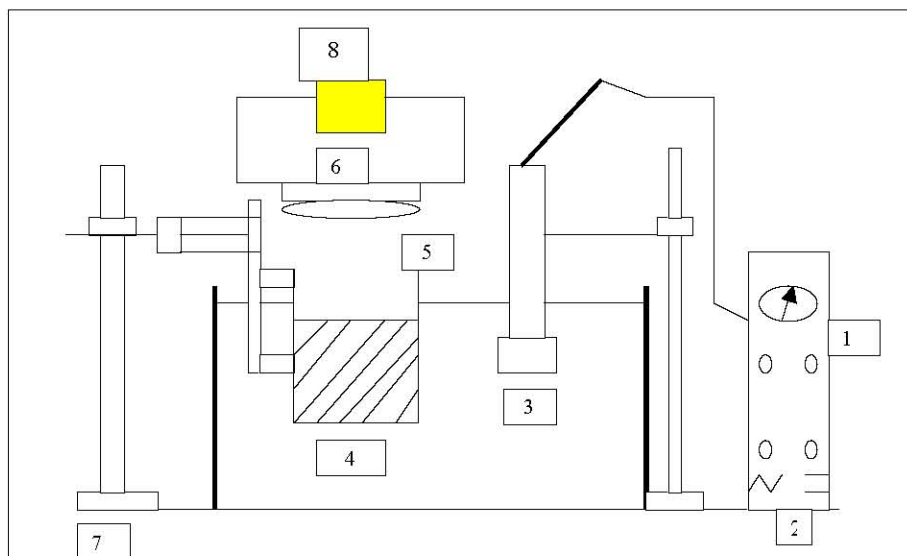


Fig. 1: Schematic Diagram of The experimental apparatus System
1-on off KeY, 2-ultrasonic generator, 3-cavitation Probe, 4-waterbath, 5-vessel, 6-UV Lamp, 7-Stand, 8-Power supply:

(b) Total organic Carbon (TOC) was determined with MSDS MO 174 TOC vials (HACH) incubated during 120 min at 100°C in COD reactor and measured colorimetrically in HACH DR/2000 Spectrophotometer. The evaluation methods were performed using the methods described by APHA [19].

(c) High performance liquid Chromatography (HPLC) was performed with HPLC system (waters) equipped with model 600 delivery system, model (Waters 486) UV detector set at 254 nm and the data recorded by Millennium chromatography. Manger software 2010 (Waters, Milford MA 01757). Reverse phase C18 Nucleosil column 250 XY mm, 10 µm (Macherey-Nagel, CO, Germany) was used. Mobile phase: Methanol: H₂O 1:1 isocratic program, flow rate 1ml / min. For analysis, aliquots of prepared standards and tested solutions were transferred to HPLC vials and analyzed immediately.

RESULTS AND DISCUSSION

The pretreated samples showed a decrease in COD values from 960 mg/L down to 88.33 mg/L, 175.53 mg/L, 88.33 mg/L and 84.97 mg/L using O₃, K₂FeO₄, LB Mg²⁺ and zetag 92, respectively. Figure 2 illustrates the COD/TOC ratios during treatment period of time. It is shown from the data that when using ozone and potassium ferrate oxidation process is the major since COD decreased at higher rates than TOC due to degradation of all oxidizable matters such as carbon, nitrogen organic and inorganic as present in wastewater, but TOC represents degradation of only organic carbon.

Effect of Ozone Pre-treatment on Sonophotocatalysis:

Individual ultrasound waves treatment was subjected 90 minutes to wastewater samples. The ultrasound process occurs cavitation and cleavage of dissolved oxygen (into [•]H atoms and OH radicals). This process enhanced decomposition of organic compounds and oxidize or reduce inorganic compounds. This phenomenon explains the increase of COD up to 86.58% as shown in Fig. 3. The subjection for combination treatment of (US and UV) for 90 minutes shows more increase in COD value up to 87.30%. In contrary further (US and UV) 30 minutes treatment achieved a slight decrease in COD value. A continuous significant decrease in COD value reached 93.83% was achieved on subjecting sonophotocatalyses (US and UV and TiO₂) combination treatment. This can be attributed to the heterogeneous environment (TiO₂ particles) in the reaction which enhanced the production of active radicals ([•]H and [•]OH)

via cavitation leading to the oxidation of the reactants in the absence of light. Our results agreed with Petria *et al.* [20]. Besides, the degradation efficiency of (US and UV) combination treatment on TOC% removal is higher than that resulting from individual effects of US as shown in Fig. 5 up to 77.77%. While the presence of US assist the photocatalytic reaction and provides more accessible sites for photocatalytic substrates, the increase over all surface area of TiO₂ particles thereby improves the absorption of photons indicating higher TOC% removal up to 84.55%.

Effect of Oxidation with K₂FeO₄-vi Pre-treatment on Sonophotocatalysis:

Samples subjected to sonolyses 90 minutes after ferrate pre-treatment showed nearly the same trend of ozone oxidation as shown in Fig. 4. Where as, a gradual increase in COD value up to 81.1 % was achieved on the first US treatment for 90 minutes. On further combination (US and UV) treatment 90 minutes the COD value achieved increase up to 83.5%. The combination (US and UV and TiO₂) treatment activated water splitting and the presence of Fe₂O₃ in aqueous stream showed good response with reaction media and sharp decrease of COD value down to 84.74% [21].

TOC in wastewater samples achieved 85.32% removal when subjected to (US and UV) combination treatment as shown in Fig. 5. Thus K₂FeO₄-VI pretreatment enhanced the TOC removal significantly compared to ozone pretreatment that achieved 77.77% removal at the same period of time (90 min. US and UV radiation).

Effect of Liquid Bittern Pretreatment on Sonophotocatalysis:

Individual US treatment for 90 minutes showed no change in COD values as shown in Fig. 3. This may be related to the presence of Cl⁻ (anions) which affects negatively the photocatalytic degradation rate. Our results agreed with Augugliaro *et al.* [22] and Tanaka and Saha [23]. Henglein [24] declared that addition of salts increases the ionic strength of the aqueous phase, which drives the organic pollutants toward the bubble-bulk interface under sonication where majority of degradation takes place in the bubble-bulk interface and affects nucleation process and the cavitation threshold, thus enhances the overall degradation rate. However, combination treatment of (US and UV and TiO₂) showed a significant increase for COD value up to 59.69%. The increase is attributed to the PI (isoelectric point) of TiO₂ is around 6.3, so that TiO₂ particles carry positive charges thus, Cl⁻ ions can be adsorbed to the positively charged TiO₂ particle surface due to ionic force.

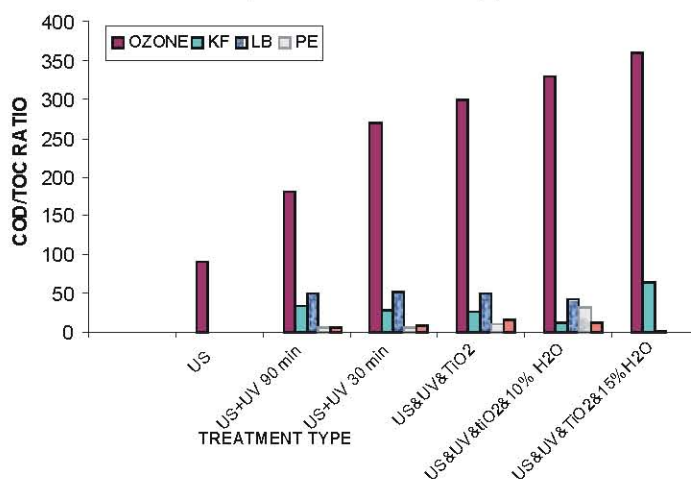


Fig. 2: The effect of ozone potassium ferate liquid bitter zetag 92 on COD/TOC ratio during degradation of energetic wastewater using sonophotocatalysis

Where: Kf = potassium ferrate oxidation, O_3 = ozone oxidation, PE = polyelectrolyte coagulation and LB = Liquid Bitter coagulation

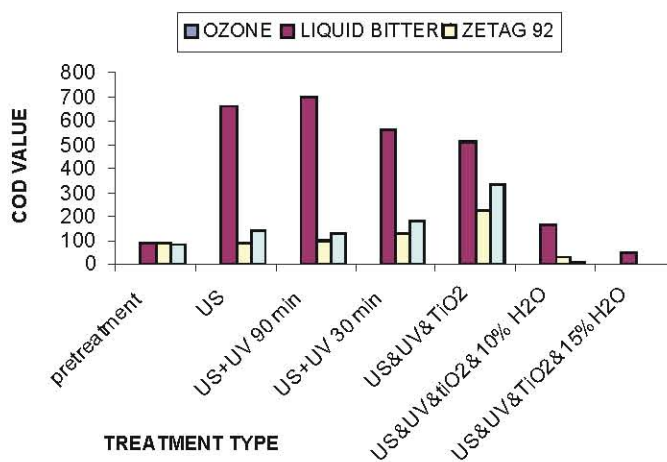


Fig. 3: Effect of ozone and liquid bitter and zetag 92 pretreatment and COD value changes on energetic wastewater degradation using sonophotocatalysis

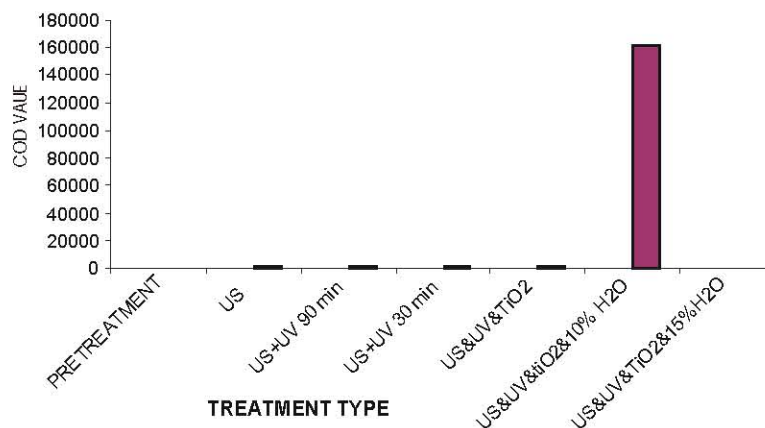


Fig. 4: Effect of $KFeO_4$, COD during degradation of energetic wastewater using sonophotocatalysis.

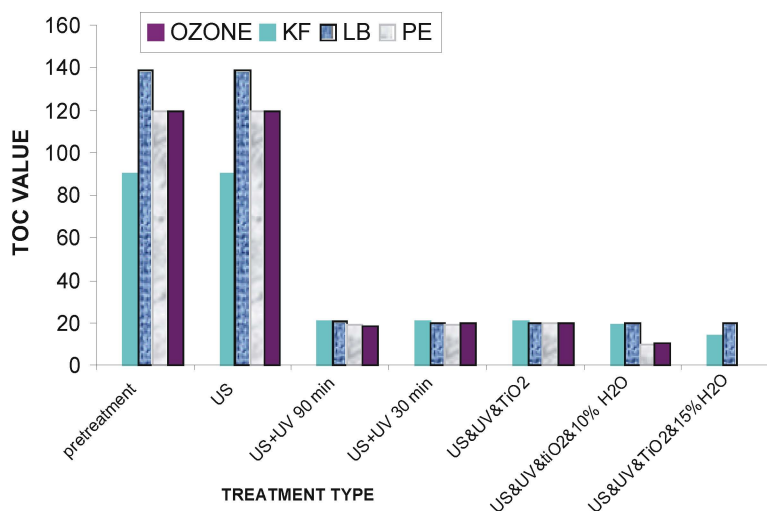


Fig. 5: Effect of ozone and potassium ferate and liquid bittern and zetag-92 pretreatment and TOC value changes of energetic wastewater degradation using sonophotocatalysis

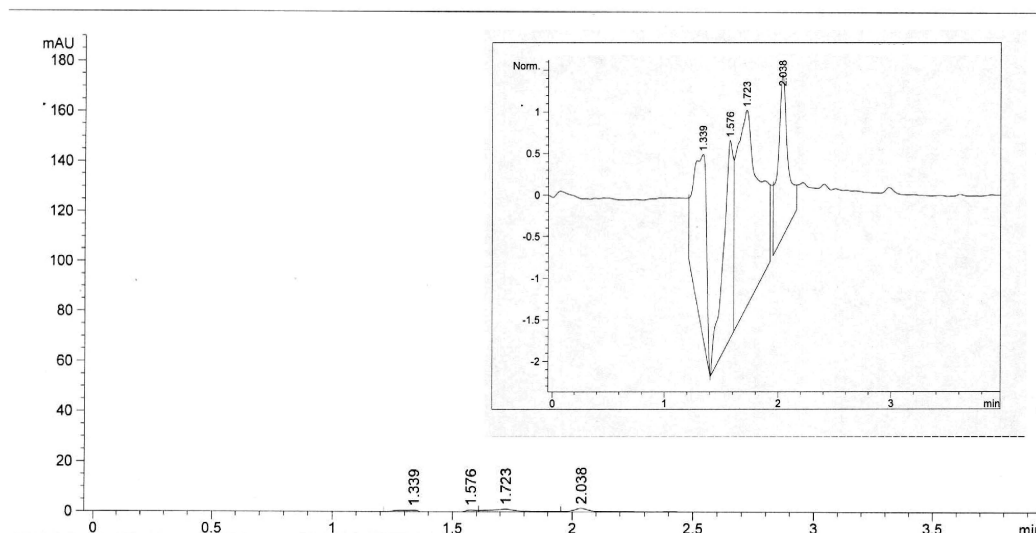


Fig. 6: Chromatogram of aqueous sample pretreated with cationic polyelectrolyte, followed by photolysis for pollutant degradation. The peaks represent (uracil, phenol, nitrotoluene and toluene) respectively

Accordingly, the reaction of surficial holes with the undesirable Cl^- ions decreases the formation of hydroxyl radicals, resulting in the low photocatalytic efficiency. On further subjection to (US and UV and TiO_2 and 10% H_2O) a significant enhancement for COD degradation was achieved indicating 86% COD removal.

TOC achieved 84.25% removal upon subjecting combination of (US and UV) treatment for wastewater samples as shown in Fig. 5. A steady state was illustrated on further (US and UV) followed by (US and UV and TiO_2) combination treatments indicating lack of $\cdot\text{OH}$ radicals. Whereas upon dilution 10% and subjecting (US and UV

and TiO_2) a significant drop in TOC value was fulfilled producing 91.9 % removal due to the increase in $\cdot\text{OH}$ radicals from water dissociation which enhanced pollutants removal.

Effect of Coagulation with Zetag 92 –Pretreatment on Sonophotocatalysis: Wastewater samples subjected to sonolysis 90 minutes showed a significant increase in COD value up to 53.67%. On further combination treatment (US and UV) 180 minutes the COD value increased up to 93.99% as shown in Fig. 3. Upon subjecting combination treatment (US and UV and TiO_2)

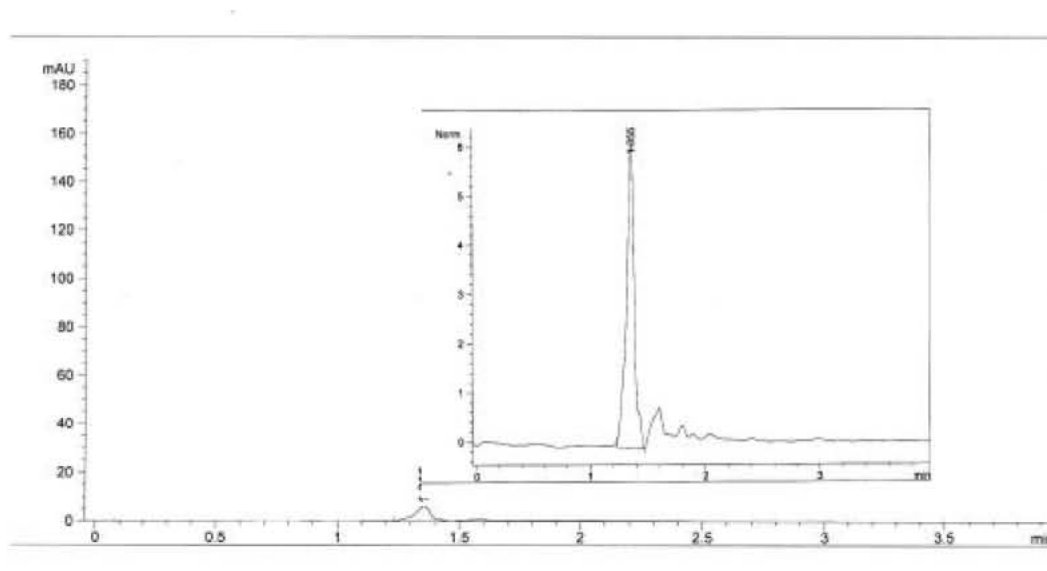


Fig. 7: Chromatogram of aqueous sample pretreated with Liquid Bittern, followed by photosonolyses for pollutants degradation. The peaks represents uracil only.

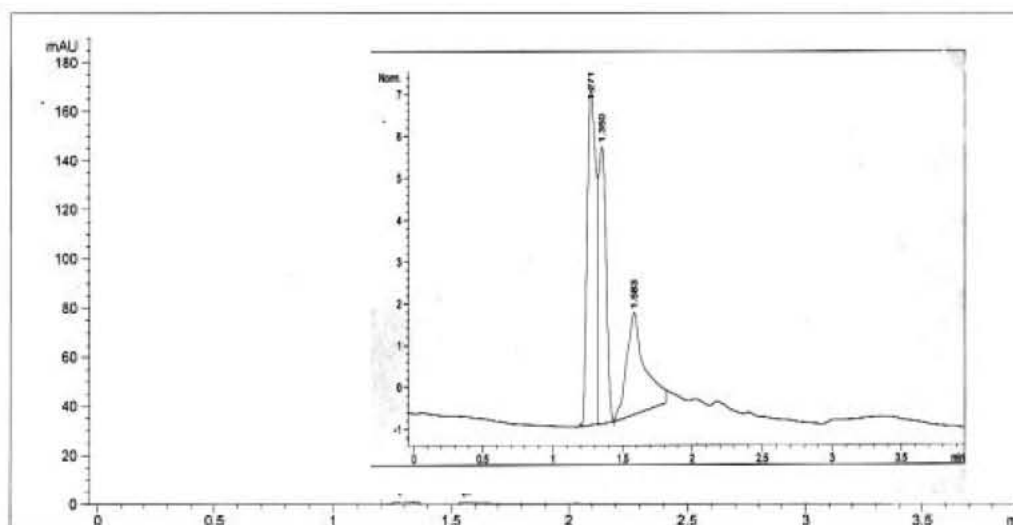


Fig. 8: Chromatogram of aqueous sample pretreated with Potassium ferrate as oxidant, followed by photosonolyses for pollutants degradation. The peaks represents uracil and phenol.

a further increase in COD value was achieved indicating no free hydroxyl groups in the reaction media. Thus, as soon as the (US and UV and TiO_2 and 10% H_2O) combination treatment was subjected a high significant COD removal was achieved up to 97.57%.

The TOC removal behavior is shown in Fig. 5 where a sharp drop in TOC value was reached by (US and UV) combination treatment 90 minutes. On further treatments such as subjecting (US and UV) or (US and UV and TiO_2) with or without 10% H_2O , the same behavior was achieved indicating removal of all pollutants.

High Performance Liquid Chromatography (HPLC): Separations of nitro aromatic products have been investigated on chromatograms with good resolution except for phenols there was a low shift in the retention time. In all chromatograms uracil and phenols were existed. The only retention time of 4-nitro toluene was observed in one chromatogram corresponding to cationic polyelectrolyte pretreatment followed by sonophotocatalysis treatment. Figure 6 showing 99.87% removal of nitro toluene. Only uracil retention time appeared, but phenol, nitro toluene and toluene

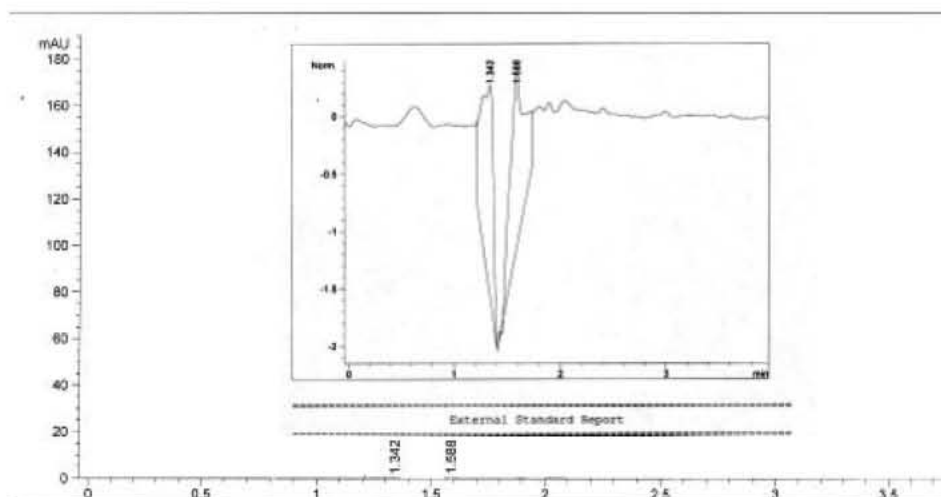


Fig. 9: Chromatogram of aqueous sample pretreated with ozone as oxidant, followed by photosonolyses for pollutants degradation. The peaks represents uracil and phenol.

disappeared completely in the chromatogram corresponding to liquid bitter (LB) as coagulant pretreatment followed by sonophotocatalysis treatment (Fig. 7). However, comparing LB coagulation pretreatment followed by sonophotocatalysis with polyelectrolyte coagulation followed by sonophotocatalysis showed that good effect of LB as only the retention time of uracil was investigated >95% removal, indicating 100% removal of all other pollutants such as (phenols, nitro-toluene, toluene). While HPLC chromatograms of polyelectrolyte pretreatment followed by sonophotocatalysis at final stage, showed the presence of retention time of uracil, phenols and nitrotoluene even at very low traces as in Fig. 6.

Comparing, oxidation states pretreatment of Potassium ferrate followed by sonophotocatalysis and ozonation pretreatment followed by sonophotocatalysis, both final treatment indicated the presence of the same retention time of uracil and phenols at the final treatment stage. Figures 8 and 9 indicating the phenol removal of 95.15% and 95.12% respectively. Thus oxidation pretreatments used with ferrate or ozone in the two HPLC chromatograms demonstrated more than 95% removal of uracil and phenols in addition to 100% removal for nitro toluene and toluene as pollutants byproducts.

CONCLUSION

- In this study the effect of sonophotocatalysis was tested for removal of pollutants contained in the wastewater after pretreatment using oxidation or

coagulation followed by sonophotocatalysis treatment.

- The coagulation pretreatment effect and sonophotocatalysis showed COD removal 97.57% and TOC removal 94.35% using cationic polyelectrolyte (zetag-92). Liquid bitter pre-treatment combined with sonophotocatalysis showed COD removal 84.74% and TOC removal 85.32% only. Ozone pretreatment and sonophotocatalysis achieved COD removal 93.83% and TOC removal 84.55%.
- High performance liquid chromatography (HPLC) was used to confirm the degree of demineralization of pollutants at the end of treatments. The HPLC chromatograms indicated that wastewater pretreated with zetage-92 still containing few traces of uracil, phenols, nitrotoluene and toluene. HPLC Chromatograms of liquid bitter pre-treatment indicated the presence of uracil only in higher content.
- While HPLC chromatograms of wastewater pretreated with ozone effect and sonophotolysis indicated lowest content of uracil and phenols. The oxidation with potassium ferrate pre-treatment and sonophotocatalysis effect is illustrated by HPLC chromatograms showing also the presence of uracil and phenols with highest content.
- Concluding that ozone pretreatment and sonophotocatalysis were the best tool for demineralization for complete TOC degradation.

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