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Innovative in Situ Technologies for Remediation of Energetics

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***Abstract*— The main purpose of the energetic materials is their reactive behavior. All their forms therefore have a footprint on human, animal, and plant systems. The demilitarization operations like Open Burn and Open Detonation, the manufacturing process and the accumulation of disposed munitions create severe contamination of water and soil and that is why it is crucial to understand and influence the caused adverse effects. Managing the munition requires knowledge and great care to avoid public concerns and comply with legislation. The objective for novel "green" energetics in the last years discovers chemical compounds and compositions, which will increasingly be used in munitions. Remediation of the contaminated area can be achieved by employing three main groups of methods: physical, chemical, and biological. Advanced oxidation processes (AOPs) are utilized in applications for which conventional oxidation methods, like chlorination, are insufficient, when process kinetics are slow, or contaminants are resistant to chemical oxidation. In some cases, pollutants become only partially oxidized, resulting in the creation of stable by-products of possibly higher toxicity than the starting substrate. Innovative AOPs using the benefits of combining different methods or utilizing different catalysts to speed up reactions are considered as competitive remediation technics during removal of complex munition pollutants resulting in easy operation and simple preservation in field. AOPs such as Fenton reactions, heterogeneous photocatalysis, Ozonation, and Electrochemical oxidation are effective in removing persistent emerging contaminants that cannot be treated by conventional physicochemical and biological methods. The results show that AOPs could be effective processes for the degradation of explosives. Utilizing in-situ treatment approach for explosive degradation has potential benefits for complete degradation of contaminants, reduced cost and infrastructure compared to traditional methods and reduced overall remediation time.**

Keywords*— *AOPs, explosives, pollutants, remediation.

I. Introduction

It is not allowed anymore to dump the munitions at sea or leave them to landfill sites. Moreover, caution must be taken to follow up and monitor the contamination of the already stored materials since metal corrosion and subsequent chemical leakage can harm. The current energetics are and will be the main environmental pollutants in the future and the remediation activities must employ new technologies for better cleaning up and restore contaminated water and soil. The chemical compositions of munitions significantly differ in their properties, generating their versatile behavior in the environment. The new direction in the environmental protection laws moves from the general statement to more precise determination like "Polluter Pays." This concept ensures that the organization or the person causing the contamination will take ownership on the cost for remediation or cleaning up. In the USA, the EPA has announced almost $1 billion to help states and territories implement PFAS testing and treatment at public water systems. This comes from a pot of $9 billion that will be available to help 'communities with drinking water impacted by PFAS and other emerging contaminants". But there is more, the EPA has made an additional $12 billion – just over €11 billion for 'general drinking water improvements, including addressing emerging contaminants like PFAS [1].

Environmental Management is the process of identifying, preventing, and mitigating the environmental impact from energetic materials. Munitions are a small part of Environmental Management, but they cannot be ignored. The environmental risks remain low and the remediation costs for contaminated land and water need to be minimized using the principle for the best available

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technology (BAT) to keep up with industry standards of environmental protection.

Referring to the data provided by The Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP), approximately 100 million pounds of energetic materials waste, or 41 percent of the total life-cycle energetic waste production, is generated during manufacture. An additional 449,000 tons of energetics waste is produced during demilitarization [2]. It is well known that almost all the explosive material is consumed during first order detonations. Second order detonations, blow in place and open burning may produce deposition of significant quantities of explosives. Thousands of buried unexploded ordnances are corroding and leaching their chemical contents into the environment. Explosives such as RDX, trinitrotoluene (TNT) and octogen (HMX) are frequently detected in soil and water and can lead to cumulative environmental consequences as heavy metals and other chemical compounds are known toxins and carcinogens. As the authors Hristo P. Hristov and Hristo I. Hristov correctly remark the explosive detonation as a chemical process which never fully completes, and it is expected that the residual energetics will be spread over broad areas [3]. There are numerous factors influencing the detonation behaviors and it is difficult to precise the complex mechanisms between the chemical compounds, the formation of residues and the influence of climate conditions. To support the assessment, a widely used framework of environmental management is used that enables identification and mitigation of environmental impacts.

The mitigation may be defined as reducing, avoiding, or offsetting any adverse environmental consequences of specific activities and can be summarized as [4]:

- Minimizing impacts by limiting the magnitude of the action and its implementation.
- Rectifying the impact by repairing or remediating the affected area.
- Reducing or eliminating the impact over time by preservation and maintenance during the life of the activity.
- Compensating for or offsetting the impact by replacing or providing substitute resources.

Physical methods like excavation and disposal are effective, their applicability is constrained by cost and logistical challenges for large, contaminated areas. Physical measures are suitable in cases when the detonation processes would not destroy the containment systems. Chemical methods, such as oxidation and reduction, focus on transforming explosives into less toxic byproducts. In biological technologies, the breakdown of explosives can take place with bacteria under aerobic or anaerobic conditions, where the explosive compound serves as a source of food. Physicochemical methods outperform biological actions, as they are faster and can be applied to a wider range of compounds. The additional benefit of possible process control flags these methods as more favorable.

In situ chemical oxidation (ISCO) is a remediation technology that involves the injection of chemical oxidants. It is important to select an appropriate oxidant, dosing, and activation agent (if needed) based on the contaminants present since not all compounds can be treated effectively by a single oxidant.

The Advanced Oxidation Processes (AOPs) is defined as the process which uses strong oxidants to transform contaminants or pollutants in the aquatic system to a less toxic or non-toxic substance by the reduction-oxidation system. One of the first definition states that AOPs are water treatment processes which occur at ambient temperature and pressure and involve generation of a powerful oxidizing agent, like hydrogen radical ($HO^{\bullet}$). Further research extended that concept to electrochemical systems generating $HO^{\bullet}$ on an anode surface under the application of high current density. Currently, as AOPs are considered degradation processes based on the generation of highly reactive oxygen species (ROS), such as hydroxyl radicals ($HO\bullet$), superoxide radicals ($O^{2\bullet-}$) and singlet oxygen (O_2). ROS participates in the degradation of organic matter, which mostly leads to the creation of CO_2 and H_2O or more biodegradable species with less environmental impact.

There are few innovative methods of generation of ROS of high potential to be applied in practice which combine the benefits of the previously known AOPs: Fenton reaction, Heterogeneous photocatalysis, Ozonation and Electrochemical process.

II. MATERIALS AND METHODS

A. Fenton reaction

Fenton process is based on an application of iron as a catalyst for improvement of oxidative potential of hydrogen peroxide (H_2O_2). Iron catalyst (Fe^{2+}, Fe^{3+}, iron oxides) is the most applied material during the Fenton process [5]. It is worth mentioning that the most appropriate material for catalytic applications besides good processing parameters is one that is easily removed from the process contaminants and should be reusable without reducing process efficiency. The basic reaction of the Fenton process runs in accordance with the reaction in Eq. 1:

$$Fe + H_2O_2 \rightarrow Fe^{3+} + \dot{O}H + OH^{-} \quad (1)$$

Hydroxyl radicals created during Fenton reaction can be utilized during decomposition of the explosive compounds. The reaction is performed at acidic conditions (pH ≈ 3), which promotes the creation of radicals.

Since nearly all explosives are manufactured by the nitration of organic compounds, the Fenton reaction is considered a promising method for organic wastewater treatment, owing to its high efficiency, simplicity, non-toxicity, and cost-effectiveness. However, there are still some limitations, such as narrow operating pH range, a large volume of iron sludge produced, an excessive amount of Fe^{2+} required, and possible corrosion of the equipment, as well as poor cost-effectiveness under high pollution load and necessity for the recovery of precipitated catalyst after the process. Moreover, the sludge can contain organic compounds and heavy metals and must be treated further. The processing of used catalysts can significantly increase overall process operation costs. The mentioned drawbacks still prevent Fenton process from widespread application. it is important to mention that the efficiency of the Fenton reaction during the treatment of water containing many various contaminants is lower comparing with its degradation efficiency with one component. This can be attributed to competition of pollutants for reactive oxygen radicals.

B. Heterogeneous Photocatalysis

The term photocatalysis describes all processes carried out with semiconductor materials. The process consists of the creation of free radicals by the interplay between photons such as those from a surface of a semiconductor and molecules of chemicals provided in the solution. The principle of operation of the process is based on the absorption of light, which subsequently induces a charge separation process with creation of positive holes. The created holes possess the ability to oxidize organic substrates of concern. During photocatalysis nanomaterials are irradiated with light, in which filled valence band, and an empty conduction band are present. When the irradiation of photon energy exceeds its band gap energy, photogenerated holes are created. These holes react with the pollutant or generate reactive oxygen species like OH^-, O_2, H_2O_2 which can oxidize organic molecules. The process of photocatalysis is depicted in Fig.1. [6].

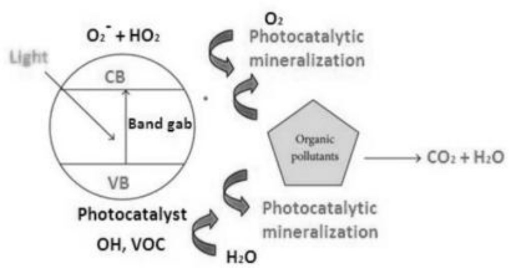

Fig. 1. The oxidation path of heterogeneous photocatalysis

One of the most important features of the application of solid catalysts is the simplicity of their separation from the reactor in most cases by filtration and their reusage without significant diminishing of activity. Photocatalysis also enables the chemical transformation of complex chemicals under mild conditions, what is in most cases unreachable using the other methods. The process can be successfully applied during wastewater decontamination, water splitting to generate hydrogen and for synthetic purposes.

A photocatalyst is a substance, which can be activated by the photon and helps acceleration of a reaction. It is important to explain that during an accelerated reaction the photocatalyst is not consumed. There are several compounds described as potentially good semiconductors, such as TiO_2, ZnO, ZnS and CdS with titanium oxide exhibiting the most promising potential for the photocatalytic application due to its non-toxicity, relatively low cost, and high efficiency. Recent research proves that metal–organic frameworks (MOFs) and graphene-based nanostructures are listed as potential photocatalysts. The application of MOFs as catalysts is still at an early stage of development and requires further investigations in terms of safe operation, lifespan, reusability, process conditions, and stability in aqueous conditions.

C. Ozonation

Ozonation is a method utilized for the degradation of inorganic or organic molecules and for inactivation of microorganisms. The method requires the generation of ozone directly during the process owing to the instability of O_3. Ozone (O_3) can be generated during the reaction of an oxygen molecule with an oxygen atom via gas discharge, photochemical excitation, and electrochemical reaction. Ozone acts as the initiator of the oxidation process and oxygen-containing products are obtained following the process. This type of method does not demand extreme conditions and can be performed at low and ambient temperatures.

Ozone is thirteen times more soluble in water than oxygen, which speeds its application in remedial works. Additionally, O_3 is highly reactive thanks to its molecule structure. Ozone is composed of three oxygen atoms, of which one is the central atom, and two others are connected to the central one by covalent bonds. Owing to that, one of the oxygen atoms is electron-deficient with electrophilic properties, whereas the other one is electron-rich with nucleophilic properties. As a result, one part of the molecule reacts preferably with unsaturated functional groups, whereas the second part reacts rather with carbonyl and carbon–nitrogen bonds molecules. O_3 possesses very reactive properties and can oxidize a wide spectrum of pollutants by direct ozonation or by an indirect reaction performed by oxygen containing radicals, generated during O_3 decomposition. The transformation of the pollutants by ozonation is performed by the two strong oxidants: molecular O_3 and hydroxyl radicals (OH^-) as presented in Fig. 2.

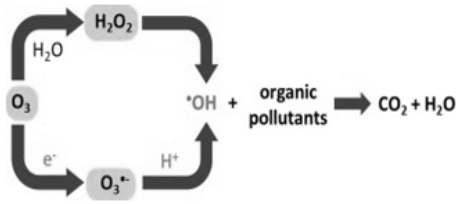

Fig. 2. The double effect mechanism of the Ozone treatment process

O_3 works as a selective oxidant and readily reacts with amines, phenol and double bounds in aliphatic compounds, whereas the hydroxyl radical (OH^-) is less selective reactant.

The efficiency of ozonation during elimination of micropollutants depends on the chemical properties of the removed compounds, operating conditions like oxidant dosage and pollutant concentration. For the successful completion of the process a comprehensive understanding is essential in the areas of the reaction kinetics, decomposition pathways, formation of by-products, and toxicity.

The main limitation of the ozonation process is low Chemical Oxygen Demand (COD) removal, which results in high ozone dosages to be utilized for treatment of substrates. The higher financial requirements are a serious obstacle during the evaluation stage. Another drawback related to the dosage is that if an O_3 dose rises above the optimal application level, a creation of toxic byproducts may occur.

D. In situ Electrochemical process

The electrochemical oxidation process converts the electric energy into chemical energy utilizing a cathode and anode placed in the environment of external electric field. This method can be divided into direct and indirect oxidation reactions. Direct oxidation takes place on the anode surface where the pollutants are adsorbed and oxidized into small molecules. Indirect oxidation generates the formation of strong oxidizing intermediates like hydroxyl radicals involved with the pollutants in the second stage of the process. Electrochemical oxidation results in good degradation of organic matter and lower chemical oxygen demand (COD) and toxicity.

The increasing challenges of the remediation of different kinds of effluents coupled with the presence of new insensitive high explosives with greater solubility drive the development of advanced technologies based on the electrochemical process. A new technology combining oxidation and reduction processes has been found to be promising in cleaning complex pollution of explosives [7]. The technology setup depicted in Fig. 3 has two columns. The reduction in the first column degrades the contaminations through nitro group reduction, transforming the nitramine compounds into more susceptible to ring cleavage and further degradation. Hydrogen peroxide is injected in the second column where in the presence of nanosized manganese dioxide catalyst and granular activated carbon is converted to hydroxyl radicals. Hydroxyl radicals, being thermodynamically active oxidants, react with nitramines and nitroaromatics in an indiscriminate approach. During the new upgraded process, the hydroxyl radicals degrade the aromatic rings into nitroaromatic compounds which was not observed in the single electrochemical oxidation method. Electrochemical reduction directly occurs at the cathode surface providing the electrochemical system with the advantage of absence of chemical reductant. These munitions containing nitro groups are susceptible to the reduction process.

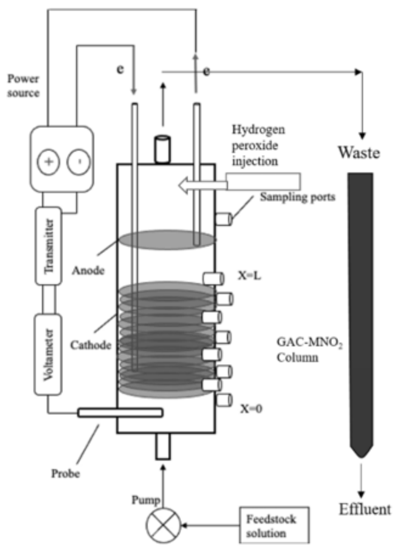

Fig. 3. Schematic of electrochemical reduction oxidation reactor with hydrogen peroxide injection

The new oxidation reduction system can be utilized in situ conditions because the low power voltage and current settings make it practical in field work. However, there are still research needs for realizing flow-through oxidative processes featuring hydroxyl radicals for explosives. The generation of hydroxyl radicals needs to be constant and sustained process, and the ease of hydrogen peroxide synthesis supports the possibility of incorporating the synthesis into the electrochemical reduction reactor. To simplify the system, direct injection of hydrogen peroxide can be suitable, but this option stays open for further research.

III. RESULTS AND DISCUSSION

The chemical nature of almost all explosives is based on organic compounds, and they exhibit extreme heterogeneity. These characteristics challenge the remediation process requesting site-specific approaches dependent upon pollutant concentration and environmental specifics. A conducted study evaluated the inhibition of the hydroxyl radical and the theory of crystal field stabilization energy. The results for all the explosives proved that the oxidation rates significantly increased with the concentration increase of Fe (II) and UV (ultraviolet) light [8]. AOPs are attractive methods for successful in-situ transformation of explosives but are not yet considered cost-effective [9].

Creative improvements based on the traditional Fenton method like Electro-Fenton technology exhibit unique advantages in versatility, high efficiency with reduced secondary contamination. Electro-Fenton has been reported as suitable for treating refractory organics. One of the most appealing advantages of Electro-Fenton is the ability to generate peroxide (H_2O_2) in situ through a two-electron transfer oxygen reduction using oxygen in aqueous solution. This ability minimizes the costs, and the risk associated with the peroxide transport while increasing the efficiency of the treatment method [10].

Another recent development of AOPs is using UV light in efforts to cost reductions. Effective removal of nitramine explosives was obtained in a trial by UV mediated method in near- neutral conditions. The effective treatment was also economical due to the replacement of electrical energy with UV light. This modification in the process achieved reduced electrical energy consumption and cost [11].

Remarkable improvements are accomplished with the implementation of metal-organic frameworks (MOFs) acting as a catalyst for the AOPs. The remedial treatment of explosives needs sustainable and economically justified solutions to remove the high concentrations of persistent pollutants. A catalyst-mediated AOPs form free radicals with high oxidizing potential speeding up the degradation process. The adaptive properties and the porous surface of MOFs suit as a catalyst of reduction and oxidation reactions. There are several combinations of compounds tailoring the properties of MOFs to achieve excellent remediation results for different applications. The treatment efficiency is controlled by alterations of the pore size. Pyrolysis is considered an appropriate method to synthesize carbon and metal oxide derivatives. It was reported that Fe_3O_4 nanoparticles adsorb contaminants with good magnetic properties. It was observed that the simultaneous addition of metal oxide derivative achieves higher degradation of contaminants. Additionally, achieving a more uniform dispersion of metal oxide in MOFs enhances the adsorbing properties of the resulting material. Adopting carbon composites like activated carbon, graphene oxide, graphite, carbon nanotubes in the MOFs framework produces large surface area for the adsorption of organic pollutants. It was found that the performance of the material is influenced by the degree of graphitization and the texture of the carbon supports. Furthermore, hierarchical pores with large specific areas allow better diffusion of pollutants [12].

IV. CONCLUSIONS

Remediating explosives requires utilizing methods that are highly efficient in treating high concentrations of organic pollutants, possible to degrade much quicker than the traditional biodegradation and not producing secondary pollutant generation. The recent research in AOPs outlines these methods as promising in situ conditions. However, the mechanism about the exact process of AOPs is still not completely investigated. The most challenging subject is to design the most appropriate AOPs system for the given pollutant at economical rates. AOPs prove excellent results with non-easily biodegradable organic compounds. To further develop their application and reduce the overall financial load the research is looking for improvements in the following:

1. Alternative and abundant energy sources for the generation of oxidant radicals like, for example, UV light.

2. Employing Electro-Fenton technology in situ condition for better cost efficiency.

3. Utilizing MOFs as a catalyst for strong adaptability, ease of operation, simplicity of design and possibility of catalyst recycling leading to cost reduction.

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