Article

Comparison of advanced oxidation processes for emerging contaminants removal

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Abstract: Emerging contaminants and their removal are subjects of growing interest. This includes endocrine disrupting chemicals (EDCs) and pharmaceutical and personal care products (PPCPs). While the adverse effects of these pollutants are documented, there remains much to be known about these contaminants. Furthermore, their removal with traditional methods has not been entirely successful. Adequate degradation can be achieved through the use of advanced oxidation processes (AOPs). Multiple factors must be considered when completing an in-depth comparison; therefore, process engineering, environmental, and economic and social parameters were included in a deeper analysis. This study used a ranking system to numerically score the performance of several AOPs (ozonation, UV, photocatalysis, the Fenton reaction, and integrated processes) in several categories of parameters. H_2O_2/O_3 presented the highest average ranking (3.45), with other processes showing similar performance. TiO_2 photocatalysis received the lowest ranking (2.11).

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1. Introduction

Numerous pollutants and toxics have been investigated throughout history, and their removal has been fine-tuned and optimized in order to achieve the highest percentage of contaminant removal at the lowest chemical and energy consumption values possible. However, not all contaminants are easily removed by traditional methods, and many remain relatively unknown. Chemicals such as these are classified as "emerging contaminants" because many are not currently regulated and have the potential to cause serious health concerns (Esplugas, et al., 2007). Many of these contaminants are actually derivatives of manufactured products, making their removal particularly complicated. Emerging contaminants have the potential to cause major effects on aquatic environments, surface water, drinking water, and soil (Miranda-García, et al., 2010). The health threat posed to both humans and wildlife has made emerging contaminants such as endocrine disrupting chemicals (EDCs) and pharmaceutical and personal care products (PPCPs) topics of particular interest (Esplugas, et al., 2007).

Some of the endocrine disruting agents include Bisphenol (preservative, plastic component); butylated hydroxyanisole (food preservative), DDT (pesticide), Atrazine (pesticide), 17β-estradiol (steroid hormone), Estrone (steroid hormone), Testosterone (steroid hormone), Cadmium, Mercury, Lead, Arsenic (heavy metals), Musk Ketone (fragrance), Hexabromocyclododecane (flame retardant) and Caffeine (stimulant). Some of the PPCPs include Acetaminophen (analgesic), Ketoprofen (Analgesic), Carbamazepine (Anticonvulsant), Ibuprofen (Anti-inflammatory), Triclosan (antobacterail), ciprofloxacin (antibiotic), acridine (antiseptic), Bezafibrate (antiepileptic), Dilantin (antiepileptic), and Nicotine (stimulant, insecticide).

1.1. *Advanced Oxidation Processes*

Due to the difficult of removing emerging contaminants, the introduction of more effective processes is necessary. Advanced oxidation processes (AOPs) have been proven as capable technologies regarding the degradation of emerging contaminants (Sichel, et al., 2011). In this process, organic compounds are fully oxidized into carbon dioxide (CO_2), water (H_2O), and mineral acids (Metcalf & Eddy, 2014). Oxidants known as free hydroxyl radicals (•OH) are formed in this process. Hydroxyl radicals react easily with organic compounds due to the unpaired electron. Large amounts of hydroxyl radicals are produced by AOPs, improving the degradation of difficult organic compounds. Furthermore, pollutants are degraded, or broken down, not simply removed or altered. Theoretically, there are no resulting products that must be removed following treatment. It follows that operational costs are reduced due to the lack of the secondary waste stream that would be present if other processes, such as adsorption, ion exchange, and stripping, were utilized (Metcalf & Eddy, 2014).

Common oxidizing agents used in AOPs include ozone (O_3), UV, and hydrogen peroxide (H_2O_2). Individual success degrading emerging contaminants has been demonstrated, but greater removal can be achieved through processes that combine multiple oxidizing agents (Metcalf & Eddy, 2014). AOPs investigated in this research include: H_2O_2/O_3, O_3/UV, and H_2O_2/UV. Several of these technologies are more widely known and well-developed, while others are more novel, such as titanium dioxide (TiO_2) photocatalysis and Fenton's reaction.

1.1.1. Ozonation

Due to its ability to cause cell lysis in bacteria, ozone (O_3) has often been used as a disinfectant. The production of ozone must occur on-site because it cannot be stored; this can have a significant effect on operational costs (Reynolds & Richards, 1996). Furthermore, concentrations of ozone that are greater than 23% are potentially explosive (Davis, 2010). Ozonation is capable of achieving 90% emerging contaminant removal, and it is the most commonly used dark oxidation method (Esplugas, et al., 2007).

1.1.2 Ultraviolet Light

Ultraviolet light has been used for disinfection purposes in the past, but its applications are extended to AOPs through the process of photolysis (Reynolds & Richards, 1996). Photolysis degrades contaminants through light exposure and the absorption of photons (Metcalf & Eddy, 2014). This absorption of photons causes the outer electrons in a compound to become unstable, and thus they become reactive or split. UV lamps are commonly used as the light source in this process, but the sun is also a viable source. Experiments have been completed to determine the advantages and disadvantages of submerged versus overhead bulbs, resulting in the conclusion that submerged bulbs produce improved effects (Reynolds & Richards, 1996). In addition, either low-pressure or medium-pressure lamps can be used. Medium-pressure lamps require a smaller number of lamps because their intensity is greater than low-pressure lamps (Davis, 2010).

1.1.3 Photocatalysis

Photocatalysis degrades a wide variety of contaminants by forming free hydroxyl radicals in the presence of a metal oxide semiconductor and a light source (Haroune, et al., 2014). Titanium dioxide (TiO_2) has been found to be among the most effective and can be utilized as either a slurry or an immobilized catalyst (Belgiorno, et al., 2007). Furthermore, photocatalysis has been found to not only degrade contaminants, but also the derivatives that are produced during most treatments (Haroune, et al., 2014). Removal efficiencies for emerging contaminants have been reported as greater than 98% in some studies (Esplugas, et al., 2007).

1.1.4 Fenton Process

During the Fenton reaction, hydroxyl radicals are formed through the reaction between ferrous iron (Fe^{2+}) and H_2O_2 (Lloyd, et al., 1997). It has been reported that the Fenton reaction is capable of removing compounds, such as clofibric acid and X-ray contrast agents, which are not removed by more common methods, such as ozonation (Esplugas, et al., 2007).

1.1.5 H_2O_2/O_3

The individual success of H_2O_2 and O_3 may be limited, but the efficiency can be significantly increased if these compounds are merged into one technique (NWRI, 2000). This combination of processes can be advantageous in some instances, such as during the degradation of compounds that do not absorb UV well (Metcalf & Eddy, 2014). Furthermore, H_2O_2/O_3 has an advantage over UV processes because of the lack of related equipment and maintenance, which can reduce energy requirements.

1.1.6 O_3/UV

Another viable integration of processes is O_3/UV. Ozone photolysis first produces H_2O_2. The H_2O_2 can then react with the O_3 to produce hydroxyl radicals for use in contaminant degradation. The multiple mechanisms simultaneously contribute to the efficacy of this process because there are opportunities for degradation through not only the production and reaction with hydroxyl radicals, but also through ozonation and photolysis (Metcalf & Eddy, 2014).

1.1.7 H_2O_2/UV

Hydroxyl radicals can also be produced through the photolysis of H_2O_2. However, high dosages of both UV and H_2O_2 may be necessary. Subsequently, high amounts of H_2O_2 may be present in the effluent. This can impede disinfection and requires removal. Despite this fact, it has been found that elevated H_2O_2 concentrations can be used to degrade pollutants that were not able to be degraded by UV treatment alone (Linden, et al., 2004). As previously mentioned, processes related to the use of UV lamps are subject to fouling and higher energy consumption costs. However, the lack of the use of O_3 can be considered an advantage because there is no potential bromate production (NWRI, 2000).

2. Results

2.1 Process Engineering Parameters

Mechanical reliability, process reliability, flexibility, adaptability, and energy consumption compose the process engineering parameters. Table 1 displays the rankings assigned to each of the processes for each parameter and the average rankings for each process. These findings are summarized in Figure 1.

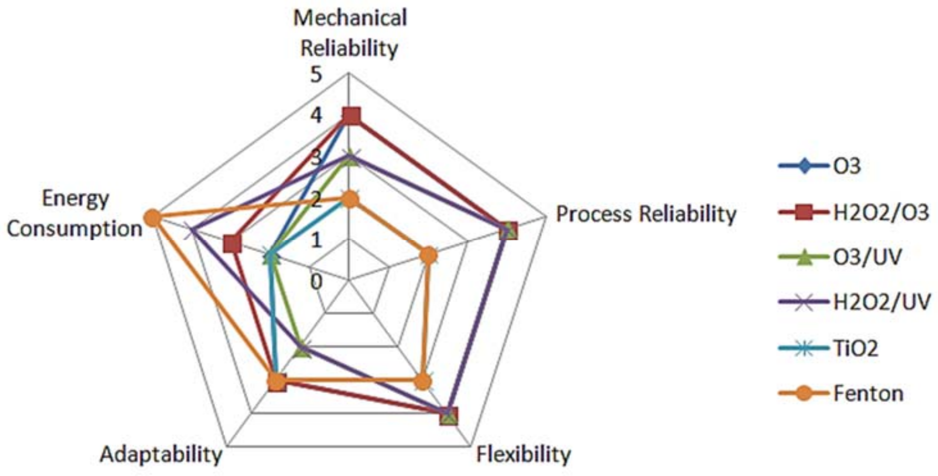

Figure 1: Process Engineering Parameters

Table 1: Parametric Ranking Summary

	AOPs					
Parameters	O_3	H_2O_2/O_3	O_3/UV	H_2O_2/UV	TiO_2	Fenton
Mechanical Reliability	4	4	3	3	2	2
Process Reliability	4	4	4	4	2	2
Flexibility	4	4	4	4	3	3
Adaptability	3	3	2	2	3	3
Energy Consumption	2	3	2	4	2	5
Average Engineering	3.4	3.6	3	3.4	2.4	3
Climate Change	2	3	2	4	2	5
Eutrophication	5	5	5	5	5	5
Toxicity	2	3	2	3	2	2
Average Environmental	2.25	2.75	2.25	3	2.25	3
Public Acceptance	4	4	4	4	2	2
Ease of Use	4	4	4	4	2	2
Economic Feasibility	5	4	4	3	1	4
Average Economic and Social	4.33	4	4	3.67	1.67	2.67
Comprehensive Average	3.33	3.45	3.08	3.36	2.11	2.89

Contribution to climate change, eutrophication, terrestrial and aquatic toxicity/degradation products are the environmental parameter in consideration. The rankings assigned to each of the processes for each parameter are found in Table 1. Figure 2 compares these findings graphically.

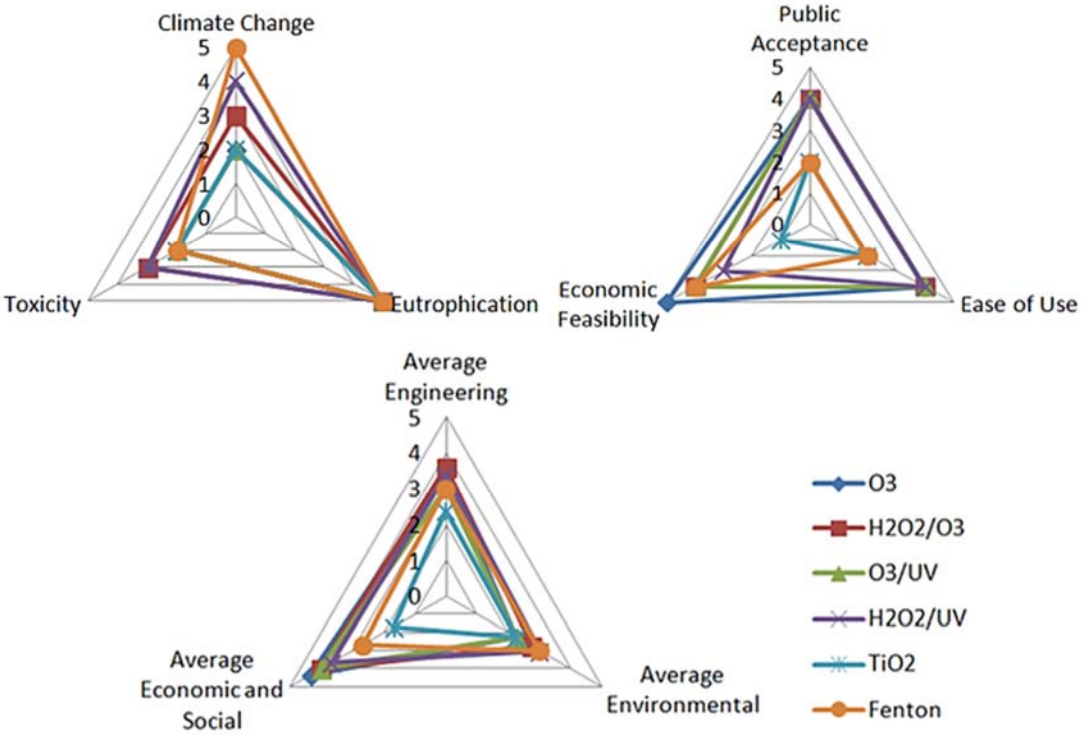

Figure 2: Environmental, Economic and Social Parameters and Comparison of Average Rankings

Thus, rankings of four for O_3, H_2O_2/O_3, O_3/UV, and H_2O_2/UV can be seen in Table 1. While TiO_2 photocatalysis and the Fenton reaction are newer technologies, they are also fairly flexible. These processes are often designed in semi-batch reactors, suggesting that they can manage flow rate fluctuations, which earns them rankings of three (NWRI, 2000). Operation and maintenance costs include costs relating to part replacement, labor, analytical methods, chemical use, and electrical requirements (Mahamuni & Adewuyi, 2010). Estimates were not found for H_2O_2/O_3, so a comparison between related technologies was used to assign ranking. Ozonation performs incredibly well in this area, particularly in comparison to the other processes. TiO_2 photocatalysis, however, shows little strength relating to economic feasibility as it reported a total cost of $8648/1000 gallons (Mahamuni & Adewuyi, 2010). Somewhat average rankings were assigned to the remaining methods. Ozonation received a very high score for its low cost of $1.023/1000 gallons (Mahamuni & Adewuyi, 2010).

3. Discussion

Throughout this study, the comparison being made between more established processes and more modern processes is a major issue to consider. TiO_2 photocatalysis and the Fenton reaction often times received lower scores because of their relative novelty, while the more conventional processes received higher scores. This is especially true amongst the economic and social parameters. This may not be a fair comparison, as the general public is becoming more open to new technology, so the negative reflection illustrated in this study may not be accurate. In addition, vastly different results could be found if this same study was completed in the future.

It can be difficult to create an equal comparison between all of the processes discussed. One key component for consideration is the constituent matrix of the influent to be treated. Some pollutants are more readily degraded than others; therefore, processes removing these contaminants may be more likely to produce high rankings. Also, some pollutants react more positively to some processes. An examination of all processes across multiple source waters would be advantageous.

Degradation products created through these processes are also a concern, particularly because they are prospectively more harmful than their parent products. Detection and identification of transformation byproducts is essential as these could have more detrimental effects on humans and the receiving environment (Gomez, et al., 2008). Additional research is needed to achieve a better understanding of these byproducts, as well as to determine the correct mechanisms of removal.

4. Materials and Methods

4.1 Holistic Analysis

A holistic analysis was completed using three categories: process engineering parameters, environmental parameters, and social and economic parameters. Process engineering parameters include: mechanical reliability, process reliability, flexibility, adaptability, and energy consumption. Environmental parameters include: contribution to climate change, eutrophication, terrestrial and aquatic toxicity, and degradation products. The selection of these parameters were influenced by the factors investigated during Life Cycle Analysis studies. Social and economic parameters include: public acceptance, ease of use, and economic feasibility. A variety of AOPs were studied, including: O_3, H_2O_2/O_3, O_3/UV, H_2O_2/UV, TiO_2 photocatalysis, and the Fenton reaction

4.2 Parameter Ranking Methodology

A ranking system was created to assign a numerical value corresponding to each process's performance in the parameters. This system compares the processes and parameters on a uniform, numerical basis. The highest positive value possible is represented by a ranking of five, while a value of one indicates the poorest performance. Application of the ranking system allows for comparison of each process for the individual parameter. Average rankings were also calculated for each category of parameters, which indicates the process that performs at the highest level in each category. The technologies that function well in all three categories were identified by a cumulative comparison. A final average ranking could then be calculated using the category averages, essentially indicating the superior technologies overall.

5. Conclusions

Advanced oxidation processes have successfully demonstrated their ability to degrade emerging contaminants. This includes: O_3, H_2O_2/O_3, O_3/UV, H_2O_2/UV, TiO_2 photocatalysis, and the Fenton reaction. Performance based on engineering process parameters, environmental parameters, and economic and social parameters was examined to complete a more robust study. A ranking system was used to compare these processes. Ultimately, H_2O_2/O_3 achieved the highest ranking at 3.45. O_3, O_3/UV, H_2O_2/UV, and the Fenton process received similar average rankings (3.3, 3.08, 3.36, and 2.89

respectively), while TiO_2 photocatalysis achieved the lowest ranking at 2.11. However, these rankings are not an absolute indication of advantage because some parameters must be considered as more influential. Economic and social parameters caused the most significant variation in scores due to electrical costs.

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