Supercritical water oxidation of toxic waste generated in veterinary practices

Abstract

The preservation of anatomical samples is a critical step in the veterinary practices. For this purpose, formaldehyde diluted in water is commonly used. It is deposited in large ponds where the pieces are placed. The problem is that in Colombia this chemical is considered as a pollutant by the environmental forensic authorities, due its properties and the damage that it can be caused to the water resources if it is not treated before to disposal. To treat this waste and prevent legal problems it was selected the supercritical oxidation technique. This method is highly efficient in destruction of toxic organic compounds. The samples were obtained from the Anatomical Lab of La Salle University in Bogotá-Colombia. The best result was an efficiency of destruction of 99.51% using 500°C, 5 min and 100 % H\textsubscript{2}O\textsubscript{2}. Excess. It permitted the reduction of COD from 9200 mg L\textsuperscript{-1} to 40 mg L\textsuperscript{-1}, allowing the compliance of the regulation and indicating that the method is effective for the treatment of this kind of waste in a batch reactor.

Keywords: formaldehyde, supercritical water oxidation SCWO, anatomical labs waste

Abbreviations: SCWO, Supercritical water oxidation; COD, chemical oxygen demand

Introduction

Fixation is a crucial step in the veterinary practices that involve preservation procedures to anatomical pieces to prevent decomposition. Fixation helps to preserve cellular architecture and composition of cells in the tissue to allow them to withstand subsequent processing. Fixation also preserves the proteins, carbohydrate and other bio-ac moieties in their spatial relationship to the cell, so that they can be studied.\textsuperscript{1} Formaldehyde has been the most commonly fixative substance used to prevent decomposition of anatomical pieces and is used in addition as fungicide, germicide, and industrial disinfectant, making it a pollutant of sanitary interest, due to its solubility y in water, generating high risk for water resources.\textsuperscript{2} The environmental forensic authorities must check that this chemical has not dump into the sewer system of this kind as conventional waste without prior treatment. To prevent legal problems this research, propose SCWO, that is a process developed for organic waste treatment. To prevent legal problems this research, has not dump into the sewer system of this kind as conventional waste and prevent legal problems it was selected the supercritical oxidation technique. This method is highly efficient in destruction of toxic organic compounds. The samples were obtained from the Anatomical Lab of La Salle University in Bogotá-Colombia. The best result was an efficiency of destruction of 99.51% using 500°C, 5 min and 100 % H\textsubscript{2}O\textsubscript{2}. Excess. It permitted the reduction of COD from 9200 mg L\textsuperscript{-1} to 40 mg L\textsuperscript{-1}, allowing the compliance of the regulation and indicating that the method is effective for the treatment of this kind of waste in a batch reactor.

Methods

Reagents

a. Hydrogen peroxide 50%

b. Formaldehyde 37 %

Sampling

It was performed an appropriate sampling used the method described in the IDEAM manual (Environmental Authority in Colombia). In-situ parameters such as temperature, pH and solids were measured and then the sample was kept in a refrigerator. Subsequently the sample was transported to the laboratories of Environmental Engineering at La Salle University in Bogota, where analysis of COD, fats and oils, TSS and pH for identifying the composition of the sample were performed.

Design and construction of the reactor

The construction of the reactor was carried out with a high-pressure tubing 1/4 “(0.635 cm) external diameter and a thickness of 0.035” (0.0889 cm) Swagelok brand. This type of pipe and the design of two elastic splints dampens temperature changes occurring during starting and stopping of the trial, it helps eliminate leakage related to thermal expansion and contraction.\textsuperscript{6} To assemble the reactor a segment of 34 cm was cut to insert it into the muffle, and then was sealed reactor with a set of nuts and ferrules on each end, following the directions of assembly provided by the brand used, placing the nut into the tube, then the two braces, which are manually adjusted to the maximum.

Then, using the press was set the male screw and nut with a wrench with ¾ back is adjusted (Figure 1).\textsuperscript{6}
Experimental design

The experimental methodology was 2k factorial design in which the temperature (A), percent excess oxidant (B) and the time (C) are handled as variables, to study how these three affect the reaction. Because k is the number variable to evaluate the experimental methodology, it was run a factorial design 2^3. Eight tests were conducted, each of them with a replica, additionally three levels were used: high, middle and low studied, which resulted in 20 tests with the results obtained in each test an analysis of variance, with which the influence of each of the variables in the treatment took place was determined. The range of variables, were established from the literature review on supercritical oxidation technique. Temperature between 400°C and 500°C. Oxidation time between 5 and 20 minutes. Excess hydrogen peroxide between 100% - 300%. Experimental domain of a continuous factor expressed with the minimum and maximum values that can take, and the coded notation to the lower level -1 and +1 was assigned to the upper (- and + for simplicity). To determine the volume to be injected into the reactor was taken into account the available volume within it, the excess percentage of peroxide oxygen, fluid density to the experimental temperatures were determined through open access program “Chemalogic steam tab”. Taking as volume injected 0.76 mL, 0.93 mL and 1.41 mL, at temperatures of 500°C, 450°C and 400°C respectively. Additionally, the composition of the mixture between the sample and the oxidant varies depending on the percentage of excess and the fluid density in supercritical temperature (Table 1) (Table 2).

| Table 1 Dimensions and reactor design |
|---------------------------------------|
| **Inside diameter** Dint= Dext- (2*espesor) |
| Dext (cm) | 0.635 |
| Thickness (cm) | 0.035 |
| Dint (cm) | 0.565 |
| **Cross Area** A = (π(Dint) *2)/ 4 |
| Dint (cm) | 0.565 |
| Cross Area (cm²) | 0.251 |
| **Reactor volume** V=A*h |
| Cross Area (cm²) | 0.251 |
| Length (cm) | 34 |
| Total volume of the reactor to normal conditions (cm³) | 8.5 |

Experimental analysis

Several preliminary tests were conducted to establish the variable values to use; for that purpose, a synthetic sample was made and was carried to supercritical conditions with reaction time in the range of 5 to 30 minutes, temperature variation between 300 to 500°C and oxidizing agent from 100% to 300% of excess. Once the ranges of the variables were found, 16 experimental tests were made a sweepstakes in order to determine the order of trials and ensure their representativeness and randomness (Table 3), and were made the same procedure described in the preliminary tests. With the ranges established for experimentation it was determined that the experimental tests included a temperature variation between 400 to 500°C. Reaction Times in the range of 5 to 20 minutes and Hydrogen Peroxide (H₂O₂) was selected as an oxidizing agent from 100 to 300% of excess of the stoichiometric reaction of destruction of formaldehyde. For tests, the solution to be injected was prepared corresponding to each of the trials using micropipettes 100μl and 1000μL for introducing the fluid into the reactor. The same experimental procedure was conducted for both preliminary tests and experimental. The source providing the proper temperature for each experimental procedure was conducted for both preliminary tests and experimental. The source providing the proper temperature for each test was a muffle furnace in which the reactor was introduced with the corresponding security measures, which were characterized by the use of forceps, gloves bait and Industrial mask. The reactor should be within the stove while carrying out the test, in order to ensure the reaction time (Figure 2). Upon completion of the time required for the test the reactor is removed with rapier and is necessary to cool it, for this reason the reactor placed on a piece of wood for about 15 minutes to avoid thermal shock and damage of the ferrules of the reactor.

Then, the reactor was cooled with water from the center to their splints to extend the useful life of this. Finally, with the help of the press and a wrench we proceed to unscrew the game splints one end.
of the reactor to collect the sample in a test tube with micropipettes. After each test, should be noted the importance of cleaning the reactor prior to the completion of each test in order to avoid cross contamination. Tracking the removal efficiency was measured by means of COD (chemical oxygen demand) in the Hach equipment. The analytical method for the determination of COD is the method 8000 which handles ranges between 3-170 mg/L and 20 to 1500 mg/L.

For COD determination of tests dilutions were made with deionized water of each sample in order to obtain the volume required for the COD parameter which corresponds to 2 ml. With the results of the experimental test the appropriate analysis of variance in order to determine the most important variables in the process was conducted, and whether the supercritical oxidation is an efficient technique for the treatment of liquid waste generated in veterinary practices.

Table 3 Test experimental results

| Testing | Label | T°C (A) | t min (B) | % H₂O₂ (C) | Initial COD mg/L | Final COD mg/L | Conversion % | Average % |
|---------|-------|---------|-----------|------------|------------------|----------------|--------------|-----------|
| 1       | l     | 400     | 5         | 100        | 8532             | 156            | 98.17        | 96.88     | 97.53     |
| 2       | a     | 500     | 5         | 100        | 8532             | 40             | 99.53        | 99.48     | 99.51     |
| 3       | b     | 400     | 20        | 100        | 8532             | 52             | 99.39        | 99.77     | 99.58     |
| 4       | ab    | 500     | 20        | 100        | 8532             | 106.7          | 98.75        | 98.71     | 98.73     |
| 5       | c     | 400     | 5         | 300        | 7955             | 76             | 99.04        | 98.92     | 98.98     |
| 6       | ac    | 500     | 5         | 300        | 7955             | 84             | 98.94        | 99.37     | 99.16     |
| 7       | bc    | 400     | 20        | 300        | 7955             | 76             | 99.04        | 99.04     | 99.04     |
| 8       | abc   | 500     | 20        | 300        | 7955             | 16             | 99.8         | 98.05     | 98.93     |

Results and discussion

The results of eight experimental trials with the respective duplicates are described below, each assay is determined based on Table 4. The initial COD of 9200 mg L⁻¹ and the best final COD of 40 mg L⁻¹ of the anatomy lab sample. The percentage conversion is by decreasing the concentration of COD. The COD of each test varies depending on the mixture of the oxidizing agent and the sample. Regarding the results in the experimental tests (Table 2), A and B tests were the best with 99.51 and 99.58 % removal efficiency respectively indicating that the method is effective for the treatment of this kind of waste in a batch reactor. However, the best conditions for carrying out the test is 500°C, 5 min and 100% H₂O₂. Excess in the test Figure 3A because even though the temperature of 40°C represents a lower energy cost, it must be held for 20 minutes, while temperatures over 500°C requires 5 minutes only (The higher the temperature, the lower the required time, and the lower the temperature, the higher the time required). The analysis of each variable used in the study indicates that that the temperatures used in the study are equally efficient to degrade the chemical, because the differences are small between them. Figure 3B shows that the best conversions are in 5 and 20 min; indicating that the minimum time used can be selected as the time to remove the contaminant. B, and % H₂O₂ in Figure 3C indicates that the minimum excess of oxidant is convenient to make the removal of formaldehyde. However, this analysis must be completed with a 2x2x2 Analysis of Variance, results of this analysis are in the tables below (Table 5–9): These results show that the interaction between Time and Temperature are the most significant relationship in the removal of formaldehyde because this interaction is the only one with P less than 0.05 and F is difference than the other values. As is observed in the table the tree variable interaction tends to be significant in addition to A and B.

Table 4 Experimental Variables

| Variable       | High (+1) | Low (-1) | Medium (0) |
|----------------|-----------|----------|------------|
| Temperature (°C) | 500       | 400      | 450       |
| Time (min)     | 20        | 5        | 12        |
| H₂O₂ Excess (%) | 300       | 100      | 200       |

Table 5 Data entry

| Data Entry | A1 | A2 |
|------------|----|----|
| C1         | 98.17 | 99.04 |
| C2         | 98.92 | 99.48 |

| B1         | 98.75 | 99.8 |
| B2         | 98.71 | 98.05 |
Figure 3 Relation between Conversion % and the variables used in the study (A) Temperature (°C), (B) time (min), (C) % H$_2$O$_2$.

Table 6 Values of N ABC

|       | A1 | A2 | C1 | C2 | C1 | C2 |
|-------|----|----|----|----|----|----|
| B1    | 2  | 2  | B1 | 2  | 2  |    |
| B2    | 2  | 2  | B2 | 2  | 2  |    |

Table 7 Mean values ABC

|       | A1  | A2  | C1  | C2  | C1  | C2  |
|-------|-----|-----|-----|-----|-----|-----|
| B1    | 97.53 | 98.98 | B1 | 99.505 | 99.155 |
| B2    | 99.58 | 99.94 | B2 | 98.73 | 98.925 |

Table 8 Values of AB-AC-BC

|       | A1   | A2   | AB   | AC   | BC   |
|-------|------|------|------|------|------|
| B1    | 98.22 | 99.33 | 98.7912 |
| B2    | 99.31 | 98.8275 | 99.0688 |

|       | A1   | A2   | AC   | BC   |
|-------|------|------|------|------|
| B1    | 98.55 | 99.1175 | 98.835 |
| B2    | 99.01 | 99.04 | 99.025 |

|       | A1   | A2   | BC   |
|-------|------|------|------|
| B1    | 98.52 | 99.155 | 98.835 |
| B2    | 99.07 | 98.9825 | 99.025 |

|       | 98.79 | 99.0688 | 98.93 |

Table 9 ANOVA summary

| Source | SS   | df | MS   | F    | P    |
|--------|------|----|------|------|------|
| A      | 0.35 | 1  | 0.35 | 1.09 | 0.32699 |
| B      | 0.31 | 1  | 0.31 | 0.97 | 0.353526 |
| C      | 0.14 | 1  | 0.14 | 0.44 | 0.525771 |
| AB     | 2.43 | 1  | 2.43 | 7.59 | 0.024866 |
| AC     | 0.29 | 1  | 0.29 | 0.91 | 0.368045 |
| BC     | 0.53 | 1  | 0.53 | 1.66 | 0.233614 |
| ABC    | 1.61 | 1  | 1.61 | 5.03 | 0.055187 |
| Error  | 2.54 | 8  |      |      | 0.32 |
| Total  | 8.2  | 15 |      |      |      |

Conclusion

Regarding the best result in the experimental tests was “A” test with 99.51 % removal efficiency indicating that the method is effective for the treatment of this kind of waste in a batch reactor. The best conditions for carrying out the test is 500°C, 5 min and 100% H$_2$O$_2$ Excess.
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Conflict of interest

We have the Journal’s policy, and the authors of the study certify that there is no conflict of interest.

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