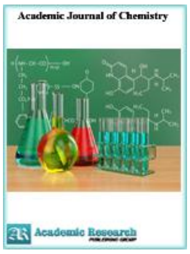

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Wet Oxidative Degradation of Cellulosic Wastes: Decomposition of Waste Protective Clothes Simulate

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Abstract:. Wet oxidative degradation is a simple treatment process based on the degradative action of hydrogen peroxide solution on the organic part of the waste and then its oxidative action on the degraded moieties converting the waste to carbon oxides and remaining secondary waste solution that contains some inorganic residues. In this study wet oxidative degradation of waste protective clothes simulate as a component of organic solid waste was performed at ~100oC and 760 mm Hg under different experimental conditions. (e.g. different weights of solid waste simulate: 35% hydrogen peroxide solutions ratios, type of catalyst and different concentrations of the catalyst used). Elemental Analysis and Infrared spectroscopy (IR) were used as tools to follow up the degradative and oxidative actions of 35% hydrogen peroxide on the protective clothes waste as a component of the solid cellulosic waste. Keeping the amount of 35% hydrogen peroxide added constant and increasing the weight of the protective clothes accompanied by detectable decreases in weight reduction and conversion percentages.

Keywords: Cellulosic waste; Oxidative degradation; Hydrogen peroxide; Weight reduction; Catalysis; Infrared analysis.

1. Introduction

Throughout the course of routine operations of the biological, medical, agricultural, research, geological explorations, quality control in construction, metal processing, oil refining projects, nuclear power plants and the decommissioning of reactors technologies a considerable amounts of mixed hazardous solid wastes were produced. The release of these dangerous wastes to the surrounding environment causes a detectable damage of the natural resources and pollutes air, water and land. This in term affects negatively the man's health and destroy the environment deprive the coming generations from a clean life. It is clear that surface disposal facilities will not accept all the waste volumes produced and will in fact receive a small amount of the total activity [1]. Therefore, these hazardous wastes must be collected, treated and conditioned before their final disposal. The primary considerations in the all treatment processes are to minimize the waste volume and, in turn the cost of the subsequent immobilization and storage processes. Health and safety of population as well as protection of the environment are additional challenges facing the designers and operators of the waste treatment technologies.

Various techniques have been suggested for treating mixed hazardous solid wastes and include incineration, pyrolysis, compaction, molten salt process, acid digestion and others [2-6].

Low temperature wet oxidative degradation technique has been developed and applied for the treatment of the organic combustible solid mixed hazardous wastes [7-12]. The majority of these wastes are made of natural materials like wood, paper, clothes [2].

The contaminated protective clothes constitute is one of the most important cellulosic solid hazardous wastes and in some cases represented to about 20% from the weight of solid waste produced [13].

In this study, wet oxidative degradation of the waste protective clothes simulate was carried out at ~100^{o}C and atmospheric pressure (760 mm/Hg) using 35% hydrogen peroxide as oxidant. The investigations of some parameters that may influence the process (e.g protective clothes to H_2O_2 ratios, type of catalyst, concentration of catalyst…) were carried out on bench scale laboratory experiments.

This study is a part of program carried out at the Inorganic and Applied Chemistry Unit, Radioisotope Department, Atomic Energy Authority, Egypt, aiming at the treatment and immobilization of intermediate and low level radioactive wastes.

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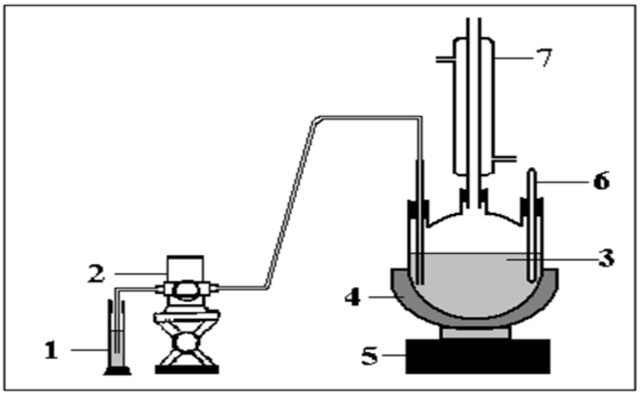
2. Experemental Work

The system used for the oxidative degradation process is consisted of three necks one liter flask, condenser, metric pump, magnetic stirrer and heating mental site supplied with thermometer, Fig (1). The matrix of the waste protective clothes simulate,(PCS), under investigation is mainly cellulosic moieties. The PCS have been shredded to facilitate the destruction process. The adapted process employs the aqueous hydrogen peroxide (35%), as oxidizing agent at ~100^{o}C. The oxidant was fed at the addition rate (1ml/min) under the surface of shredded PCS, that suspended in water (PCS : water ratio equal to1:6 wt/wt). To optimize the destruction process different concentrations of ferrous sulphate or copper sulphate (Analar grade) were used as catalyst in batch scale experiments. The catalyst was added before the beginning of the degradation process. After a predetermined time the addition of hydrogen peroxide was stopped but the heating was continued for more two hours to ensure the complete destruction of hydrogen peroxide added. At the end of the heating period, the system allowed to cool filtrated and the weight of solid residue and the volume of the secondary waste solution were determined.

Fig-1. System used for oxidative degradation of spent protective clothes



1- 35% H_2O_2
2- Liquid pump
3- Cellulose-based waste simulate
4- Heating mantel
5- Magnetic stirrer
6- Contact thermometer
7- Condenser

IR and Elemental analysis were used as analytical techniques to follow the route of the oxidative degradation process. Hence the carbon content and IR analysis for solid residues as well as for liquid secondary waste solutions were performed.

3. Results and Discussion

Wet oxidative degradation process of solid organic radioactive waste in H_2O_2 and/or iron or copper salts catalysis systems is considered as an acceptable technique for the relatively high volume and weight reductions. In addition a detectable improvement in the immobilization of secondary waste streams in inert matrices was reached [14].

Hydrogen peroxide plays the key role in oxidative degradation process of organic solid wastes. The decomposition of hydrogen peroxide supposed to take place through the following reaction steps:

$$\mathbf{H_2O_2 \longrightarrow H_2O + O^{\cdot}} \qquad \mathbf{(1)}$$

$$\mathbf{O^{\cdot} + O^{\cdot} \longrightarrow O_2} \qquad \mathbf{(2)}$$

The combination of oxygen atoms is extremely rapid reaction and the observed rate of this reaction corresponds to the unimolecular reaction takes place in the first step, which proceeds more slowly [15].

The data represented in table (1) show the effect of increasing the weight of PCS, keeping the amount of hydrogen peroxide added constant, on the weight reduction percent, conversion percent and the destruction rate values. Although there was a reasonable increase in the destruction rate, g/min, yet detectable decreases in both weight reduction and conversion percentages were reached. This attributed to the sharp decrease in the available H_2O_2 for degradation and oxidation processes of the solid waste simulate from 43 milliliter H_2O_2 per gram protective clothes to 7.2 milliliters H_2O_2 per gram PCS. Table (1).

Table-1. Oxidative Degradation of Solid Cellulosic Wastes (Protective Clothes Simulate). Effect of increasing weights of solid protective clothes on: Destruction Rate, Weight Reduction and Carbon Conversion Percentages.

Weight of protective clothes simulateg	**Carbon content g**	**H_2O_2**		**Remain Solid Residue**				**Destruction rate , g/min ($x10^{-2}$)**
		ml/g solid waste	**ml/g carbon added**	**Weight g**	**Carbon g**	**Weight Reduction %**	**Conversion %**	
5.0	2.10	43.00	102.40	1.3495	0.533	73.01	74.62	1.70
7.5	3.15	28.70	68.25	2.3585	0.9422	68.55	70.09	2.39
10.0	4.20	21.50	51.19	2.7185	1.0697	72.82	74.28	3.39
15.0	6.30	14.30	34.13	6.0440	2.4478	59.71	61.15	4.17
20.0	8.40	10.75	25.60	6.6885	2.7356	66.56	67.43	6.19
25.0	10.50	8.60	20.48	11.4265	4.7991	54.29	54.29	6.31
30.0	12.60	7.20	17.06	13.690	5.4486	54.37	59.60	7.59

Up to73% weight reduction percent and 74% conversion percent were obtained for protective clothes simulate decomposed by 35% H_2O_2 only. These figures are less than that obtained for other cellulosic solid waste decomposed using the same technique and under the same experimental conditions. Where more than 96% and ~99% weight reduction and conversion percentages for filter paper [10] and tissue paper [11] were reached respectively. This may explained on the basis that: when cotton cellulosic fibers are subjected to mercerization treatments, during textile manufacture, the molecules structure of the cellulose are modified in such a way that although it undergoes slight chemical degradation, yet it retains higher strength [16]. This reflects also on the amount of 35% H_2O_2 consumed for decomposing the protective clothes simulate where 12.795 liters of 35% H_2O_2 (396.2 g/l) were need for destruction of the one kg of PCS which compared with 11.18 liters and 10.75 liters were required for destruction of one kg of filter paper [10] and for one kg tissue paper [11] respectively. Low temperature wet oxidative degradation process takes the advantages of high reactive radicals such as $HO^{\cdot}$, $O^{\cdot}$, …. generated from the decomposition of the oxidants ,i.e hydrogen peroxide .This decomposition can also take place through a metal ion catalysis [14]. Ferrous sulphate ($FeSO_4$ .7 H_2O) or copper sulphate ($CuSO_4$ .5H_2O) were used as catalyst to enhance the oxidative degradation process of PCS. It is clear from the data obtained in table (2) that using ferrous sulphate as a catalyst, slight decreases in both weight reduction and conversion percentages were reached. When hydrogen peroxide added to PCS –ferrous sulphate mixture the following reaction supposed to take place [17]:

$$\mathbf{Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\cdot} + HO^{\cdot} \qquad (3)}$$

The pH of the PCS slurry in water at 100 ^{0}C is about 4. At this pH the Fe^{3+} begin to precipitate as hydroxide and hence the catalyst ions were not be freer for oxidation/reduction reactions. This consequently results in slight decrease in the weight reduction and conversion percentages. Table (2). On the other hand using copper sulphate as a catalyst resulting in high weight reduction and conversion percentages. Table (2). Cupric sulphate is very soluble in water and at 100 ^{0}C about 75 grams dissolve in 100 grams of water [18]. When H_2O_2 added to the PCS and copper sulphate slurry the following reactions postulated to take place:

$$\mathbf{Cu^{2+} + H_2O_2 \longrightarrow Cu^{+} + HOO^{\cdot} + H^{+} \qquad (4)}$$

Cuprous salt is presumably soluble in water, but they are instantly decomposed by it to yield cupric salt [18].

$$\mathbf{Cu^{+} \longrightarrow Cu^{2+} \qquad (5)}$$

Hence the availability of soluble Cu^{2+} / Cu^{+} system may enhance the oxidation of the organic solid waste by hydrogen peroxide and consequently detectable increases in both conversion and weight reduction percentages were obtained. Table (2).

Table-2. Oxidative degradation of Solid Cellulosic Wastes (Protective Clothes Simulate). Effect of Type and Concentration of Catalyst on Weight Reduction and Carbon Conversion Percentages.

Catalyst		**Remain solid residue**							
g/g waste $X10^{-3}$	**g/g carbon $X10^{-3}$**	**Weight g**		**Carbon g**				**Conversion %**	
		$FeSO_4$	**$CuSO_4$**	**$FeSO_4$**	**$CuSO_4$**	**$FeSO_4$**	**$CuSO_4$**	**$FeSO_4$**	**$CuSO_4$**
Zero	Zero	6.6885	6.6885	2.7356	2.7356	66. 56	66. 56	67.43	67.43
1.25	2.94	9.2000	0.9900	3.6662	0.1356	54. 00	95.05	56.35	98.37
2.50	5.88	8.9200	0.5694	3.6706	0.0555	55. 40	97.15	56.30	99.33
5.00	11.75	8.3600	0.8340	3.4401	0.0717	58. 20	95.83	59.06	99.14
7.50	17.65	7.8300	0.8440	3.1263	0.0291	60. 85	95.78	62.85	99.65
10.00	23.53	7.5300	0.9190	3.0647	0.0505	62. 35	95.41	63.52	99.39

$HOO^{\bullet}$ radical formed during the reaction [4] enhanced the O_2 production according to the following reaction [14]:

$$\mathbf{HOO^{\bullet} + H_2O_2 \longrightarrow O_2 + H_2O + HO^{\bullet}} \qquad \mathbf{(6)}$$

These reactive $HO^{\cdot}$ radicals react with organic carbon of the solid waste ,(19), to yield organic radicals which oxidized by O_2 (14) .

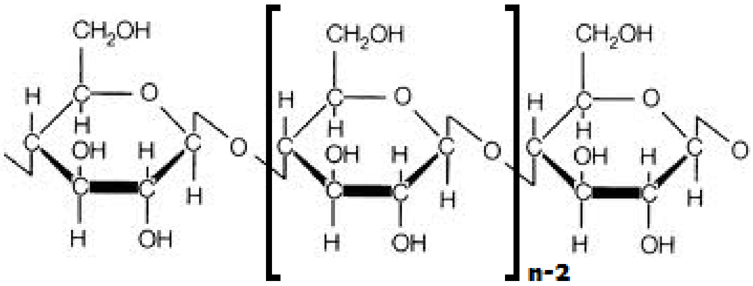
$$\mathbf{RH + HO^{\bullet} \longrightarrow H_2O + R^{\bullet}} \qquad \mathbf{(7)}$$
$$\mathbf{R^{\bullet} + O_2 \longrightarrow RCOO^{\bullet}} \qquad \mathbf{(8)}$$
$$\mathbf{RCOO^{\bullet} \longrightarrow R^{\bullet} + CO_2} \qquad \mathbf{(9)}$$

The concentration of organic carbon on the residual secondary waste solution resulting from decomposition process is a determined factor in the practicability of the subsequent immobilization process of these residues especially in cement matrix. It is clear from table (3) that using copper salt as a catalyst results in a secondary waste solution with relative low percentage of organic carbon compared with that using iron salts as a catalyst or when the oxidation process carried out in absence of catalyst. This again favorite the use of copper salt as a catalyst. Table (3).

Table-3. Oxidative Degradation of Solid Cellulosic Waste (Protective Clothes Simulate). The Carbon Content of Secondary Waste Solution as a Function of Catalyst Type and Concentrations.

Catalyst Added x 10 $^{-3}$		**Carbon content in secondary waste solution, %**	
G/g solid waste	g/g carbon	$FeSO_4$	$CuSO_4$
Zero	Zero	4.1	4.1
1.25	2.94	2.15	1.0
2.5	5.88	2.0	1.75
5.0	11.75	2.5	0.9
7.5	17.65	2.15	1.1
10	23.53	2.25	0.85

The cellulose materials consist of macromolecules of at least several hundred to several thousands of anhydrous glucose units. These units molecules condensed and linked linearly by means of 1,4 glucoside bonds as follows:



Every bond involves the potential aldehyde group of glucose unit and hydroxyl group of another. Each anhydroglucose unit of cellulose molecule has three hydroxyl groups, which are located in position 2,3and6. Each cellulose molecule is ended with hydroxyl group and aldehydic group. The cellulosic chains are linked together through hydrogen bonding exist between hydroxyl groups of one chain with another hydroxyl groups in the other. [16-20].

Hydrogen peroxide always contains a peroxide bond (-O-O) in which at least one oxygen atom is active. The production of molecular oxygen has been correlated with oxidation of cellulose and its degradation [21]. It is clear from the equations [7-9] previously stated that oxidative degradation of protective clothes simulate results mainly in water and carbon dioxide. To confirm these results, IR as a non-destructive technique was carried out for the untreated PCS as well as for the solid residues and the secondary waste solutions resulted from the batch–scale destruction experiments. The data obtained for IR analysis were represented in table (4) and shown in figs (2-8) The IR spectrum of untreated solid PCS shows an extremely intense O-H stretching frequency centered on 3300 cm^{-1} due to the broad band spreads 3400 – 3200 cm $^{-1}$ .This due to the free and/or bonded O-H groups. Part of the absorption in this region may be due to the water of the sample. Band near 2900 cm^{-1} is due to the C- H stretching vibration in the cellulosic units .The stretching frequency of C=O due to the degraded fiber in the clothes appears near 1780 cm $^{-1}$ .The sharp bands near 1650 cm^{-1} observed is due to C=O aldehydic group in cellulose .The C H_2 scissors motion in the cellulosic fibers appears near 1430 cm^{-1} ,while the bands near 1370 cm^{-1} and 1260 cm^{-1} are due to C – H stretching vibration in the cellulose units. The band near 1160 cm^{-1} has been interpreted as asymmetric C-O-C bridge stretching vibration frequency while that at 1100 cm^{-1} is due to C-O- deformation. Fig (2). Similar bands assignments for cellulosic materials were obtained in the previous literatures [22]. IR spectra of solid residues obtained from batchwise oxidative degradation experiments of different PCS: hydrogen peroxide ratios and those for using different type and / or concentrations of catalyst are represented in table (4) and in figs (3-5). It is clear from these spectrograms that the band assignments for the all spectra are nearly identical and similar to that of untreated wastes solid simulate. This favors the end wise homiletic scission mechanism for the degradation and oxidation processes of protective clothes simulate. Due to this mechanism, hydrogen peroxide degrades first the solid matrix then oxidizes the degraded moiety [11]. On the other hand the spectra of the secondary waste solutions obtained from these batchwise experiments are shown in table (4) and in figs (6-8). The most predominant bands present in all these spectra are those due to the stretching vibration of O-H groups of water of aqueous secondary waste solution and appear near 3492-3430 cm^{-1}. On the other hand bands near 1638 cm^{-1} may be attributed to –O-H deformation in water [22]. Figs (6-8).

Fig-2. IR-absorption spectrum of untreated protective clothes waste simulate

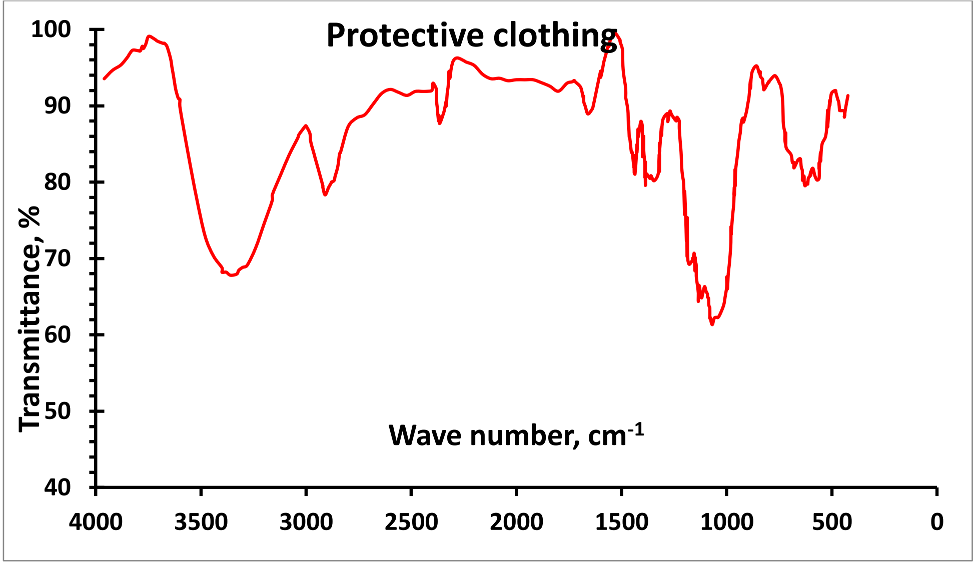


Fig-3. IR-absorption spectrum of solid residue resulting from oxidative degradation different ratios of protective clothes by H_2O_2

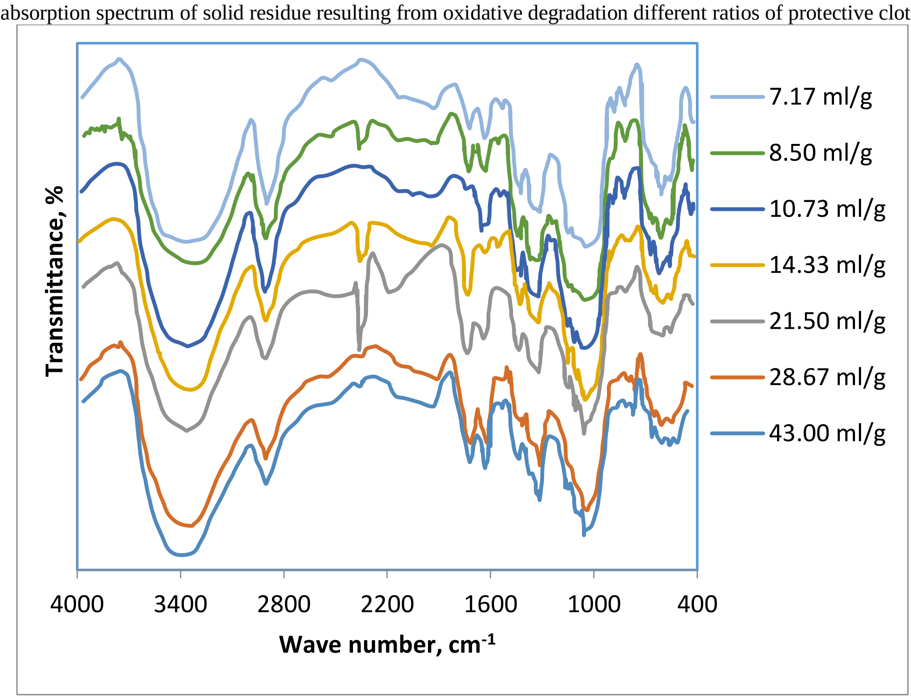


Fig-4. IR-absorption spectrum of solid residue resulting from oxidative degradation of protective clothes by H_2O_2 in presence of different concentrations of ferrous sulphate as a catalyst

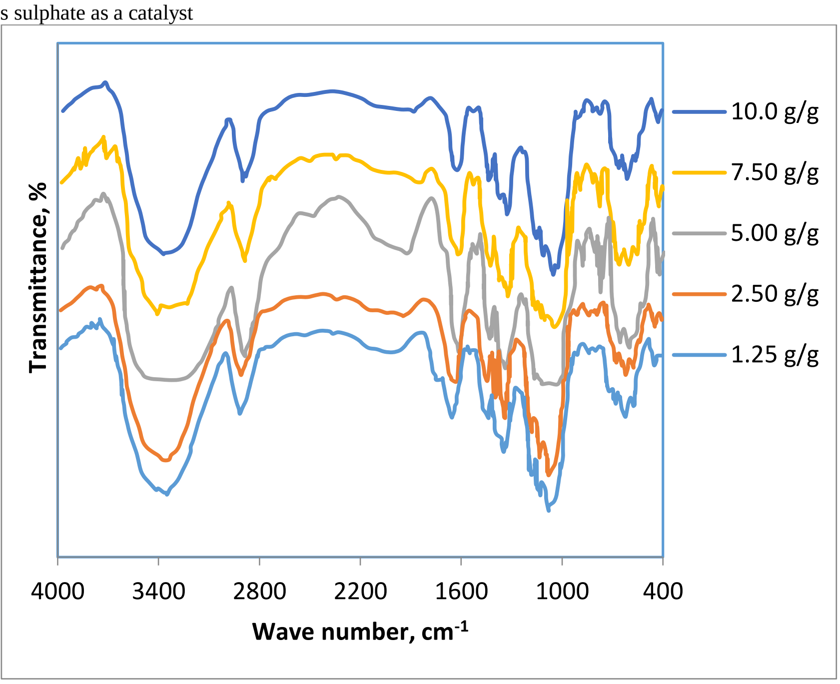


Fig-5. IR-absorption spectrum of solid residue resulting from oxidative degradation of protective clothes by H_2O_2 in presence of different concentrations of copper sulphate as a catalyst

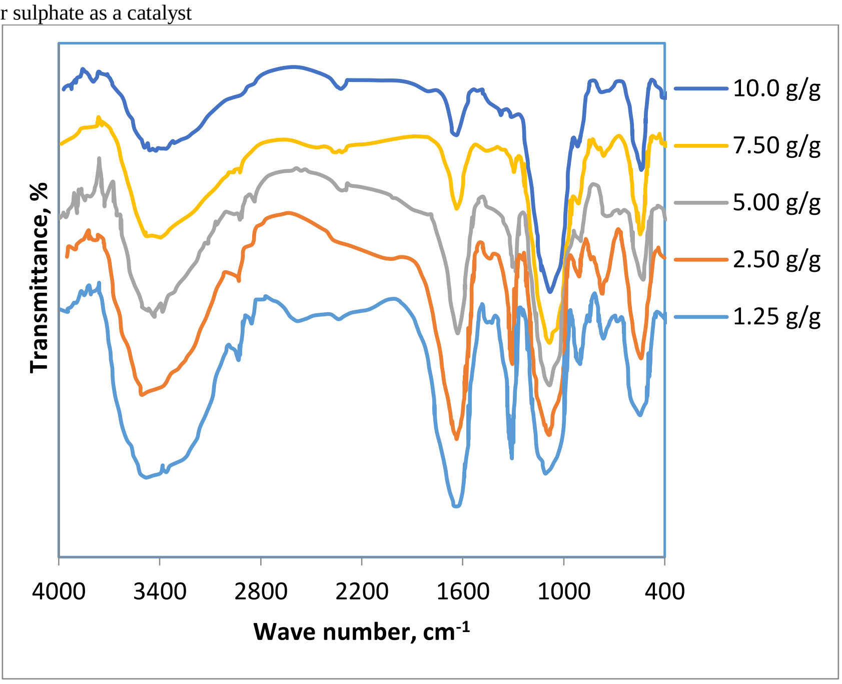


Fig-6. IR-absorption spectrum of filtrate resulting from oxidative degradation different ratios of protective clothes by H_2O_2

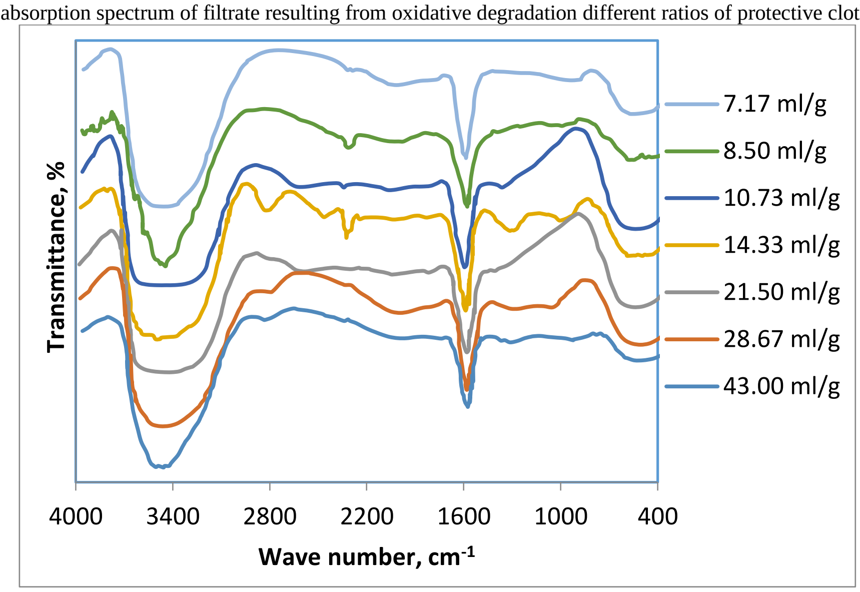


Fig-7. IR-absorption spectrum of filtrate resulting from oxidative degradation of protective clothes by H_2O_2 in presence of different concentrations of ferrous sulphate as a catalyst

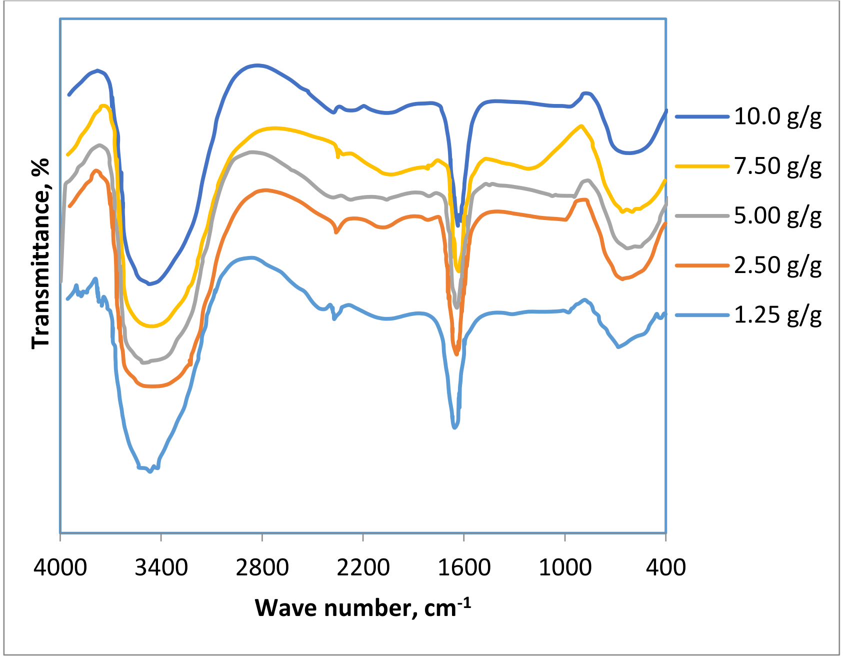


Fig-8. IR-absorption spectrum of filtrate resulting from oxidative degradation of protective clothes by H_2O_2 in presence of different concentrations of copper sulphate as a catalyst

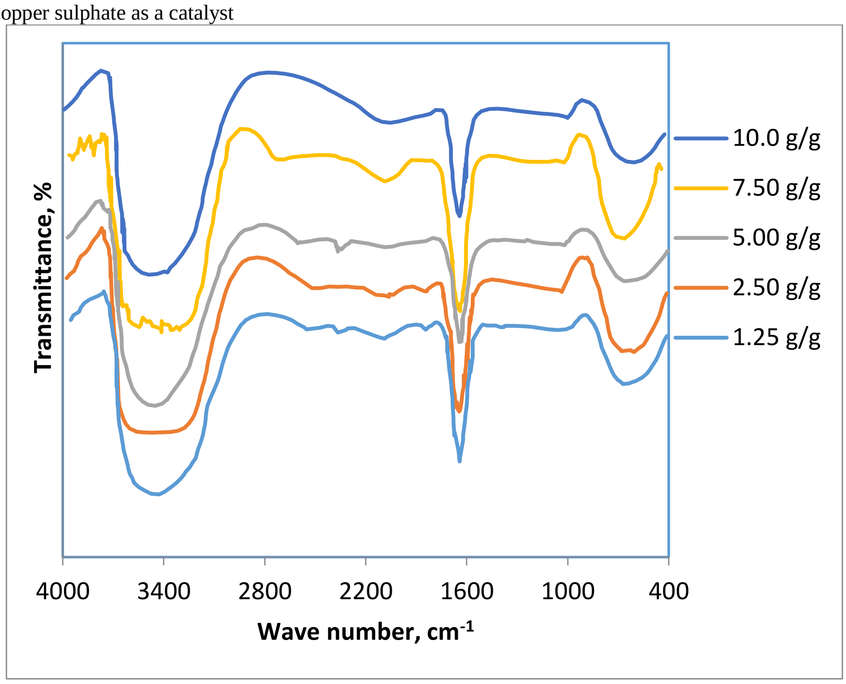


Table-4. Oxidative Degradation of Solid Cellulosic Wastes (Old Protective Clothes). The assignment of Infrared bands in cm^{-1} for untreated and treaded solid wastes Simulates.

Untreated solid protective clothes	Treated protective clothes						Band characteristic
	Solid residues			Secondary waste solutions			
	Without catalyst	Ferrous sulfate	Copper sulfate	Without catalyst	Ferrous sulfate	Copper sulfate	
3423-3284	3423-3292	3400-3336	3492-3430	3492-3430	3492-3430	3492-3430	OH str.
2900	2900	2900	2900	2845	-	-	C-H str.
1730	1730	-	-	-	-	-	C=O str.
1653	1650	1646	1653	-	-	-	C=O ald. str.
-	-	-	-	1638	1637	1638	O-H defor.
1430	1430	1430	-	-	-	-	C-H sciss
1373	1373	-	-	-	-	-	C-H str.
1264	-	-	-	-	-	-	
1160	1159	1169	1159	-	-	-	C-O-C str.
1123	1115	1115	1115	-	-	-	C-O defor.

The absence of bands indicating any intermediate products in the spectra of the secondary waste solutions confirms the proposed mechanism for the decomposition of the solid protective clothes (i.e end wise homiletic scission mechanism). Also confirms that the constituent of the secondary waste solutions is mainly water that favorite the subsequent immobilization process.

On basis of the data obtained from batchwise laboratory scale decomposition experiments of solid waste protective clothes simulate, it could be concluded that:

- The solid protective clothes wastes (as one of solid cellulosic waste) can be decomposed easily by H_2O_2 and/or H_2O_2/ Fe^{2+} or H_2O $_2$/ Cu^{2+} systems

-The cellulosic matrix that consisting the protective clothes transformed by the wet oxidative technique into an aqueous phase containing small amount of inorganic residues acceptable for subsequent immobilization process.

- Catalyzed low-temperature wet oxidative degradation process has evident superiority in organic radwastes treatment for its economy, (the only used chemical is hydrogen peroxide), moderate operation conditions (~100 ^{o}C & 760 mm/Hg) and high weight reduction (and consequently volume reduction) obtained.

- The developed wet oxidation methodology can be also applied to other organic hazardous solid and liquid wastes.

4. Conclusion

Wet oxidative degradation of cellulosic hazardous materials like waste protective clothes using hydrogen peroxide is a promising process for its advantages. High weight and volume reduction of the waste treated as well as no serious immobilization problems of the subsequent secondary wastes due to the absence of corrosive substances are the most advantages of the nominated treatment process. More than 95% of weight reduction was reached by using copper sulphate as a catalyst to enhance the oxidative degradation process.

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