

RESEARCH PAPER

INFLUENCE OF A POLYCARBOXYLATE BASED SOLUTION ON STABILITY OF HYDROGEN PEROXIDE AND APPLICATION TO E-WASTE LEACHING

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ABSTRACT

Hydrogen peroxide with its high oxidising potential is commonly used in hydrometallurgical extraction of metals from ores, anode slimes and waste materials (e.g. WEEE) and treatment of cyanidation effluents. Main detractor to H_2O_2 is its rapid catalytic decomposition leading to prohibitively high consumption. Effect of pH (0-4), Cu(II) (0-10 g.l⁻¹) and temperature (20-80°C) on H_2O_2 stability was investigated using response surface methodology. Influence of neutral-alkaline conditions (pH 7.3-11.8) and presence of solids (1-20% w/v) was also tested. A polycarboxylate based solution (PBS) was utilised to improve H_2O_2 stabilisation. The significance order of parameters on H_2O_2 decomposition was temperature > pH > Cu(II). Elevating the level of these parameters increased H_2O_2 decomposition. The activation energy (60.7±2.5 kJ.mol⁻¹) indicated a chemically controlled process. Alkaline conditions (up to pH 11.8) led to higher H_2O_2 decomposition. Presence of solids adversely affected H_2O_2 stability under certain conditions. The addition of PBS significantly improved (up to 54%) H_2O_2 stability in the presence of copper. The presence of PBS in H_2SO_4 - H_2O_2 leaching of waste of printed circuit boards (WPCBs) provided a limited enhancement in copper extraction by up to 19%. PBS can be suitably utilised to stabilise and hence reduce H_2O_2 consumption in aqueous solutions particularly in the presence of copper.

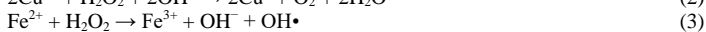
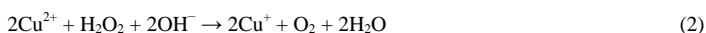
Keywords: Hydrogen peroxide; polycarboxylates; stabilization; copper; e-waste; leaching

INTRODUCTION

Hydrogen peroxide (H_2O_2) has been employed in many industrial applications due to its superior features including high oxidation potential (+1.78 V) [1], easy handling-storage and environmentally friendly nature i.e. formation of no toxic by-products during the oxidation process (Eq. 1) [2,3]. Hydrogen peroxide is extensively used in hydrometallurgical applications including leaching of gold/silver from ores to increase dissolved oxygen concentration [3,4], extraction of copper from chalcopyrite ores/concentrates as well as waste materials (e.g. WEEE) in acidic sulphate/chloride solutions under atmospheric or oxidative conditions [5-10], extraction of precious metals from anode slimes by chloride leaching [11] and precipitation of uranium and plutonium in peroxide form from pregnant leach solutions (PLSs) [12,13]. Hydrogen peroxide is also effectively used in chemical oxidation of cyanidation effluents containing free and weak acid dissociable (WAD) cyanides [14-17]. Notwithstanding this, application field of hydrogen peroxide includes waste treatment such as direct oxidation of inorganic (e.g. sulphide (S^{2-}), nitrite) and organic contaminants (e.g. formaldehyde, thiols) in drinking/natural water, oxidation of organics using advanced oxidation processes (AOP) (Fenton's process (Fe^{2+}/H_2O_2) or $H_2O_2/UV/O_3$) [3,18,19].



Despite its attributes, hydrogen peroxide is prone to catalytic decomposition resulting in increased reagent consumption, which may lead to an adverse effect on process economics [16]. For instance, in treatment of cyanide effluents (pH 10-11), despite the theoretical consumption of hydrogen peroxide for the oxidation of free cyanide is 1.31 g H_2O_2 per g CN^- , in practice, this increases by 1.5-6.1 fold [16]. Factors negatively influencing the stability of hydrogen peroxide include presence of metal ions (e.g. Fe^{3+} , Fe^{2+} , Mn, Cu^{2+} and Cr^{2+}) (Eqs. 2-3) [20-24], solids [25-26], sulphur ions (S^{2-}) (Eq. 4), thiocyanate (SCN^-) (Eq. 5) as well as the increase in temperature and pH [2,16,27]. Yazıcı and Devenci [27] demonstrated that in alkaline solutions (pH 9.5-12), increasing the concentration of copper as well as solids ratio, temperature and pH facilitate the decomposition of hydrogen peroxide.



Various inorganic/organic additives appeared to be tested in the literature for inhibition of catalytic decomposition of hydrogen peroxide by metal ions, copper in particular [22,23,26,28-31]. Many of the relevant studies focused on the improvement of the stability of concentrated acidic (stock) solutions of hydrogen peroxide (25-90% w/w H_2O_2) in order to extend shelf life of H_2O_2 products, with limited details. To the author's knowledge, there is limited work on the practical use of organic/inorganic additives for inhibition of decomposition of hydrogen peroxide in acidic/basic solutions. In a previous study, Mahajan et al. [32] showed that the addition of ethylene glycol (1-8 ml.l⁻¹) enhanced leaching of copper from chalcopyrite in H_2SO_4 - H_2O_2 solutions. Bas et al. [33] found that ethylene glycol can be suitably used as an additive in hydrogen peroxide treatment of X-ray film effluents (thiosulphate media) for silver recovery. More recently, Ruiz-Sánchez and Lapidus [34] addressed the beneficial use of ethylene glycol in the peroxide leaching of chalcopyrite mineral. The current study has been also the first attempt for improvement of copper extraction from e-waste through stabilisation of hydrogen peroxide in sulphuric acid leaching.

In this study, the effect of pH (0-4), the concentration of Cu(II) (0-10 g.l⁻¹) and temperature (20-80°C) on the decomposition of hydrogen peroxide were investigated using response surface methodology in five levels over a period of 3 h. The effects of high pHs (up to 11.8) and solids (1-20% w/v) were also tested separately. The influence of a polycarboxylate based solution (2.5-20 ml.l⁻¹ PBS) as the additive on the stability of hydrogen peroxide was also tested in much detail i.e. under different conditions of pH, temperature and solids ratio. The effect of PBS (1.3-6.7 ml.l⁻¹) on copper extraction from a waste of printed circuit boards (WPCBs) was also demonstrated.

MATERIAL AND METHODS

Tests were performed in baffled jacketed glass reactors (inner dia: 6.5 cm, 250-mL nominal capacity) connected to a water circulator (Polyscience) for maintaining the desired temperature in reactors. A multi magnetic stirrer (Thermo Scientific Variomag) was used to agitate reactors using PTFE-coated magnetic bars (diameter: 3 cm) at a stirring speed of 350 rpm. The top of the reactors was kept covered with lids over the test period.

Hydrogen peroxide solution (35% w/w H_2O_2 , Merck) and a stock solution of copper sulphate pentahydrate (200 g.l⁻¹ $CuSO_4 \cdot 5H_2O$) were used to prepare the

solutions in a final volume of 200 mL. Hydrogen peroxide was added after achieving the required temperature of the solution to prevent its decomposition before starting the test. The initial concentration of hydrogen peroxide was set at 0.5 M in all experiments. To test the effect of solids on the stability of hydrogen peroxide, quartz, which is an inert mineral (i.e. not soluble in acid/neutral/alkaline solutions) commonly present in ores, was selected. Quartz sample (>90% SiO₂, -250 μm) was firstly treated with a dilute acid solution (5% HCl, 60°C, 90 min.) to remove soluble impurities, followed by washing with distilled water. It was then dried in an oven (105°C) prior to use in the tests. A polycarboxylate based solution (PBS with a trade name of Polycar-100 produced by Iksa [35] (Table 1) was utilised as the additive to improve the stability of hydrogen peroxide. PBS is essentially a hyper plasticizer used to reduce water requirement in cement products [35]. The pH of the solutions was adjusted using either concentrated sulphuric acid solution (96%) or 4 M NaOH. All the solutions were prepared using deionised-distilled water. Samples taken at the predetermined intervals over a period of 180 min. (after centrifugation if solids were present to obtain clear supernatants) were analysed for initial and residual hydrogen peroxide with iodometric titration [36].

The addition of PBS (1.3-6.7 ml.l⁻¹) in hydrogen peroxide leaching copper from the waste of printed circuit boards (WPCBs, 18.5% Cu, 2.05% Fe) was also demonstrated. The details of the preparation of WPCBs sample can be found elsewhere [10]. Leach solutions (150 mL) containing 1 M H₂SO₄ + 1 M H₂O₂ were prepared in Erlenmeyer flasks (250 mL) prior to the addition of WPCBs sample (-250 μm) to maintain a solids ratio of 1% w/v. A temperature-controlled (80°C±1) reciprocal shaker operating at 140 rpm was used for mixing of the flask contents. Samples taken at certain intervals (i.e. 0.25 and 0.5 h) were centrifuged at 4100 rpm for 5 min. to collect supernatants for copper analysis using an atomic absorption spectrometer (Perkin Elmer AAnalyst 400). Initial and final pH, redox potentials (E_{Ag/AgCl}, mV) and hydrogen peroxide concentration were also monitored.

Table 1 Some properties of the polycarboxylate based solution (PBS)

Type	Mixture of polycarboxylate and organic salts
Colour	Light brown
Density	1.03 ± 0.02 kg.l ⁻¹
pH	6.50-8.00
Alkali content	≤ 10%
Chloride	≤ 0.1%

Design of experiments and statistical analysis of data

Effect of various parameters including pH, the concentration of copper and temperature, on the decomposition rate of H₂O₂ was investigated using design of experiments i.e. central composite design (CCD), a type of response surface methodology (RSM) [37,38]. Table 2 shows the parameters and their corresponding levels. Design-Expert software [39] was used in the calculation of regression coefficients of second-order mathematical models produced, statistical analysis of experimental data and generation of response surface plots. P-values were used for testing the significance of parameters. Simply, the null hypothesis is rejected on the grounds that the P-value is under the selected confidence level (e.g. 95%, α=0.05). This indicates that the parameter tested is statistically significant [38]. Apart from experimental design runs, additional tests were also carried out to reveal the decomposition profile of hydrogen peroxide in neutral-alkaline conditions (i.e. pH 7.3-11.8) and in the presence of solids (i.e. 1-20% w/v). Furthermore, the effect of the PBS on the stability of hydrogen peroxide was investigated in detail under different experimental conditions.

Table 2 Parameters and corresponding levels tested in the decomposition of hydrogen peroxide

Parameters	Levels				
	Lowest	Low	Center	High	Highest
A pH	-1.682	-1	0	+1	+1.682
B Cu(II), g.l ⁻¹	0	2	5	8	10
C Temperature, °C	20	32	50	68	80

RESULTS AND DISCUSSION

Modelling and statistical analysis of data

The experimental design layout with conditions for each test and corresponding responses (i.e. decomposition of hydrogen peroxide (%) at different time intervals (5-180 min.) and initial rate constants (k, min⁻¹)) is presented in Table 3. The relative standard deviation (RSD) of the experimental data was calculated to be ≤6.28%. The initial rate constants (k, min⁻¹) were calculated from the decomposition data (Table 3) using linear first-order model (Eq. 6) and also used as a response in the statistical evaluation of data (Table 3).

$$[H_2O_2] = [H_2O_2]_0 \cdot e^{-k \cdot t} \tag{6}$$

where; [H₂O₂] - instant concentration (or decomposition ratio) of H₂O₂
 [H₂O₂]₀ - initial concentration (or decomposition ratio) of H₂O₂
 k - initial rate constant (min⁻¹)
 t - time (min.)

Table 3 Central composite design (CCD) with experimental conditions and corresponding results for decomposition rates (%) of H₂O₂ at different time intervals (5-180 min.) and initial rate constants (k, min⁻¹) ([H₂O₂]₀: 0.5 M)

No	pH	Cu(II) (g.l ⁻¹)	Temp (°C)	Decomposition of H ₂ O ₂ (%)								Rate constant, k.10 ³ min ⁻¹	
				5min	15min	30min	60min	90min	120min	150min	180min		
1	0.8	2	32	1.77	1.77	1.77	1.77	1.77	1.77	1.77	1.77	1.77	1.02
2	3.2	2	32	4.76	4.76	4.76	9.74	9.74	12.2	14.7	22.1	22.1	1.08
3	0.8	8	32	1.71	1.71	1.71	1.71	1.71	1.71	1.71	1.71	1.71	3.44
4	3.2	8	32	2.20	7.07	16.8	24.1	38.6	43.4	50.7	53.1	53.1	4.42
5	0.8	2	68	12.5	10.4	11.0	17.1	27.8	42.9	48.3	55.8	55.8	4.25
6	3.2	2	68	85.0	90.0	90.1	87.8	90.4	96.7	96.7	96.8	96.8	379
7	0.8	8	68	0.98	2.93	8.53	31.6	51.6	93.5	94.7	95.1	95.1	8.10
8	3.2	8	68	85.0	85.1	85.2	85.4	88.0	90.0	90.1	90.2	90.2	379
9	0,0	5	50	3.93	4.16	4.51	5.21	10.8	11.5	21.7	22.3	22.3	1.32
10	4.0	5	50	72.5	77.5	85.0	85.1	87.7	89.2	90.2	98.9	98.9	258
11	2.0	0	50	0.87	2.61	7.92	8.60	9.28	12.4	13.0	16.0	16.0	0.88
12	2.0	10	50	7.38	7.61	12.9	35.6	45.8	55.8	60.9	68.2	68.2	6.41
13	2.0	5	20	2.14	2.14	2.14	2.14	2.14	2.14	2.14	2.14	2.14	4.32
14	2.0	5	80	80.0	91.2	91.5	91.9	91.8	92.0	92.1	93.1	93.1	322
15-				2.44	7.28	14.2	23.5	33.5	47.7	51.2	58.3	58.3	4.89
20	2.0	5	50	±0.00	±0.46	±1.25	±0.50	±1.30	±1.85	±1.36	±2.43	±2.43	±0.28

Linear regression analysis was used to calculate the rate constants (k). High correlations ($R^2 \geq 0.91$, except Exp.1 with $R^2=0.57$) showed the consistency of experimental data with the model (Eq. 6). Previous researchers [40] also confirmed that decomposition of hydrogen peroxide follows first-order reaction kinetics.

Analysis of variance (ANOVA) was applied to test the significance of regression terms (i.e. parameters) using P-values (Table 5). All the regression models were statistically significant even at a confidence level of 99.9% ($\alpha=0.001$). Linear (main) effects of pH and temperature on decomposition of peroxide at different periods and decomposition kinetics were statistically significant at the same confidence level of 99.9% ($\alpha=0.001$) (Table 5). A positive mode of effect (Table 4) indicates that increasing the pH and temperature facilitates the rate and extent of decomposition of peroxide. The effect of copper on the extent of decomposition was not statistically significant during the initial periods of 5-30 min. at 95% confidence level ($\alpha=0.05$) (Table 5). However, over extended periods (≥ 60 min.), its effect became significant (Table 4). No significant effect of copper (i.e. $P < \alpha = 0.05$) was detected on the decomposition kinetics (Table 5). The quadratic effects of pH (A^2) and temperature (C^2), and their interaction effect

(AC) on the decomposition rate and extent of H_2O_2 were found to be statistically significant at 95% confidence level ($\alpha=0.05$) between the periods of 5 and 90 min. (except for 90 min. which is significant at 90% confidence level ($\alpha=0.1$)) (Table 5).

The surface plots (Figs. 1 and 2) illustrate simultaneous effects of parameters on each response (i.e. decomposition extent (%) at 180 min. and rate constant (k, min^{-1}). High temperature and high pH appeared to aggravate the rate and extent decomposition of hydrogen peroxide (Figs. 1-2). Simultaneously, elevating the levels of pH, temperature and copper was found to produce a synergistic adverse effect on the stability of hydrogen peroxide. It is also evident from the surface plots that decomposition of hydrogen peroxide (Fig. 1) also increases with increasing the concentration of copper though its effect on the decomposition rate is relatively limited (Fig. 2). Mlasi et al. [40] investigated the effect of copper on the decomposition of hydrogen peroxide under the conditions of 1 M H_2SO_4 at 67°C. The researchers found that increasing the addition of copper sulphate by 4-fold led to a 1.74-fold increase in the rate of decomposition of hydrogen peroxide.

Table 4 Regression coefficients of the mathematical models

Terms	Regression Coefficients								Rate constant k (min^{-1})
	Decomposition of H_2O_2 (%)								
	5 min	15 min	30 min	60 min	90 min	120 min	150 min	180 min	
Constant	2.61	7.50	14.46	23.69	33.65	46.56	49.31	53.35	5.11
A-pH	20.16	21.49	22.64	21.18	20.00	17.08	16.18	17.33	86.33
B-Cu(II)	-0.23	-0.13	0.95	5.25	8.17	10.84	11.43	11.09	1.38
C-Temp.	22.26	23.65	23.44	24.58	26.12	30.38	30.19	30.20	94.85
AB	1.12	0.61	1.21	-0.31	0.35	-	-	-	-0.37
AC	19.13	19.17	17.20	11.77	6.76	-	-	-	93.18
BC	-1.11	-1.84	-2.43	-0.28	-0.93	-	-	-	-0.24
A^2	11.56	10.42	9.18	6.28	4.91	-	-	-	42.65
B^2	-0.48	-2.21	-2.97	-1.88	-2.77	-	-	-	-1.89
C^2	12.58	12.49	9.90	6.94	4.11	-	-	-	54.50
R^2 of the model	0.99	0.99	0.98	0.97	0.97	0.90	0.91	0.90	1.00

Table 5 Statistical significance of the effect of parameters and interactions on decomposition rate and extent of hydrogen peroxide (%)

Source	P - values								Rate constant k (min^{-1})
	Decomposition of H_2O_2 (%)								
	5 min	15 min	30 min	60 min	90 min	120 min	150 min	180 min	
Model	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001
A-pH	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001
B-Cu(II)	0.8343	0.9255	0.5609	0.0155	0.0025	0.0024	0.0012	0.0026	0.6405
C-Temp.	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001
AB	0.4465	0.7392	0.5690	0.8977	0.8990	-	-	-	0.9241
AC	< 0.0001	< 0.0001	< 0.0001	0.0005	0.0295	-	-	-	< 0.0001
BC	0.4526	0.3274	0.2649	0.9063	0.7334	-	-	-	0.9505
A^2	< 0.0001	< 0.0001	0.0001	0.0050	0.0330	-	-	-	< 0.0001
B^2	0.6592	0.1274	0.0811	0.3102	0.1938	-	-	-	0.5150
C^2	< 0.0001	< 0.0001	< 0.0001	0.0027	0.0652	-	-	-	< 0.0001
R^2 of the model	0.99	0.99	0.98	0.97	0.97	0.90	0.91	0.90	1.00

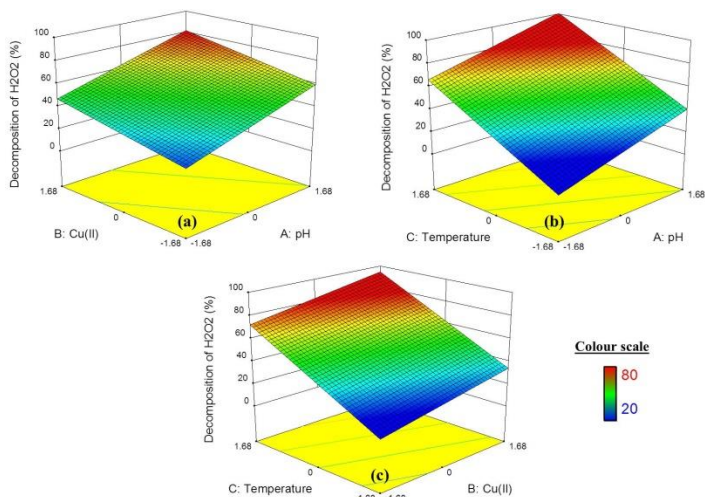


Figure 1 Response surface plots demonstrating the simultaneous effects of parameters on the extent of decomposition of H₂O₂ (at 180 min.) (the third parameter was held at centre level), (a) pH and concentration of Cu(II) (AB), (b) pH and Temperature (AC); (c) Concentration of Cu(II) and Temperature (BC) ([H₂O₂]₀: 0.5 M)

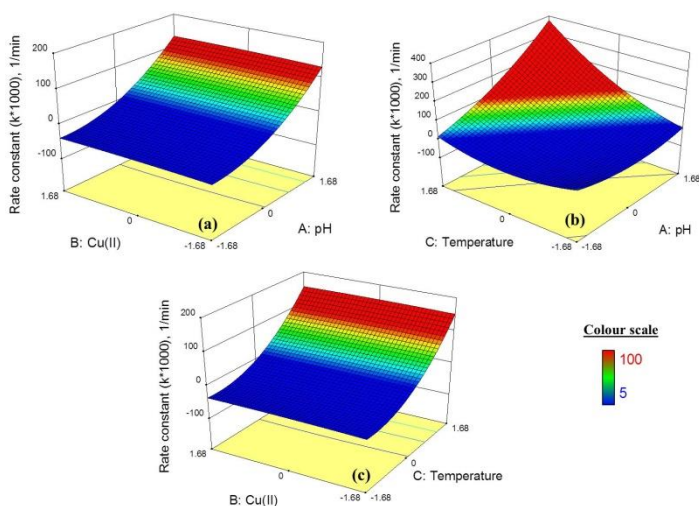


Figure 2 Response surface plots demonstrating the simultaneous effects of parameters on the decomposition kinetics of H₂O₂ (k·10³ min⁻¹) (the third parameter was held at centre level), (a) pH and concentration of Cu(II) (AB), (b) pH and Temperature (AC); (c) Concentration of Cu(II) and Temperature (BC) ([H₂O₂]₀: 0.5 M)

Considering the prime importance of temperature for the stability of hydrogen peroxide (Table 5), the activation energies (E_a) were calculated using Arrhenius equation based on the data obtained in the absence and presence of PBS (2.5-20 ml.l⁻¹) (Fig. 3). The mean value for the activation energy was 60.7±2.5 kJ.mol⁻¹ indicating a chemically controlled process (i.e. E_a>25 kJ.mol⁻¹) [41].

Decomposition of peroxide under neutral and alkaline conditions (pH 7.3-11.8) was also tested separately (Fig. 4). Elevating the pH from neutral to alkaline led to a decrease in the stability of peroxide particularly at >pH 9.8. While only ≤7.4% of peroxide decomposed at ≤pH 9.8 over 180 min., it increased to 39% at pH 11.8. Under alkaline conditions, hydrogen peroxide decomposes according to Eq. 6 [3].

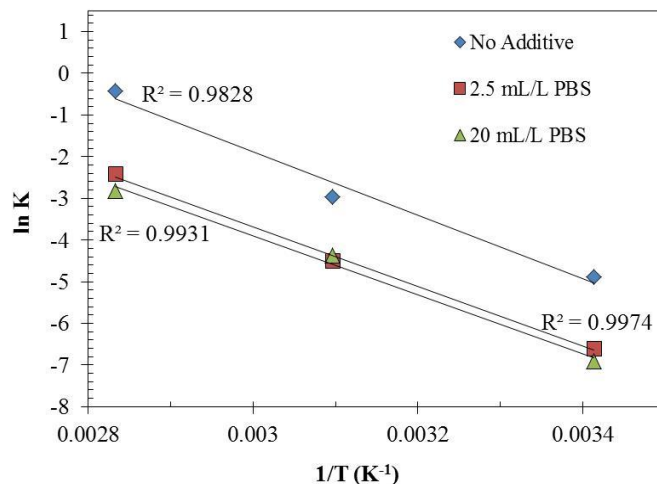


Figure 3 Arrhenius plots (ln K vs. K⁻¹) for decomposition of hydrogen peroxide in the absence and presence of PBS (2.5-20 ml.l⁻¹) (pH 4, 5 g.l⁻¹ Cu(II), [H₂O₂]₀: 0.5 M)

Consistent with the current findings (Fig. 4, Table 4-5), Yazıcı and Devci [27] reported that increasing the concentration of copper (10-40 mg.l⁻¹ Cu), solids ratio (0-4 w/v), temperature (20-50°C) and pH (9.5-12) resulted in the increased consumption of hydrogen peroxide. Lee et al. [42] compared the effects of NaOH and Na₂CO₃ for pH adjustment (pH 10.0-10.6) on the stability of hydrogen peroxide over 2 h. They found that hydrogen peroxide was relatively less stable in carbonate media since carbonate (or bicarbonate) anion promotes decomposition of hydrogen peroxide. They concluded that NaOH is a more suitable pH-modulating reagent than Na₂CO₃.

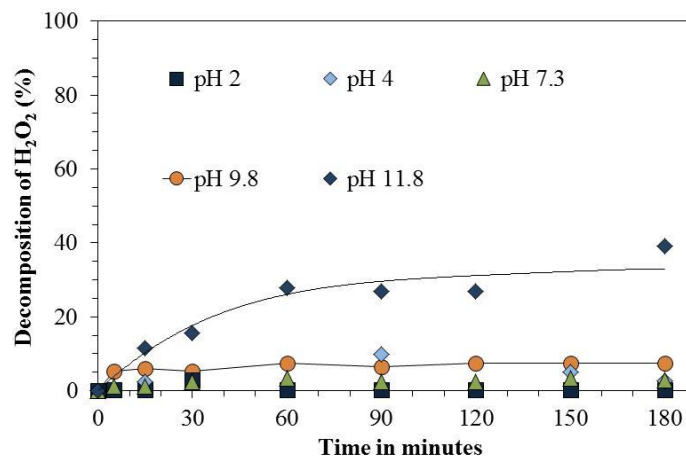


Figure 4 Effect of acid, neutral and alkaline pHs on the decomposition of H₂O₂ (%) ([H₂O₂]₀: 0.5 M, no Cu(II), 20°C)

Effect of solids

The effect of solids on the stability of hydrogen peroxide is of practical importance since solids are present in many processes (e.g. leaching of ores/metals and or treatment of pulps/effluents) where peroxide is used as an effective oxidant [6,7,16,43]. The effect of solids (1-20% w/v) on the stability of hydrogen peroxide was investigated under different pH and temperature conditions. At 20°C, the effect of solids on the decomposition of hydrogen peroxide was limited to only ≤5% at pH 2-4 over 180 min. (figure not shown). These results suggested that hydrogen peroxide is quite stable at low temperatures (i.e. 20°C) and acidic pHs (<pH 4) even in the presence of solids by up to 20% w/v. However, at high temperatures (e.g. at 80°C) a two-fold increase

in the loss of hydrogen peroxide was observed in the presence of solids (10 w/v) i.e. from 21% (no solids) to 42% (10% w/v solids) over 180 min. (Fig. 5). Yazıcı and Deveci [27] studied the effect of solids (1-4% w/v quartz) on the decomposition of hydrogen peroxide at an alkaline pH of 10.5-11. The researchers found that an increase in the concentration of solids from none to 4% w/v resulted in a 27% loss of hydrogen peroxide at 180 min.

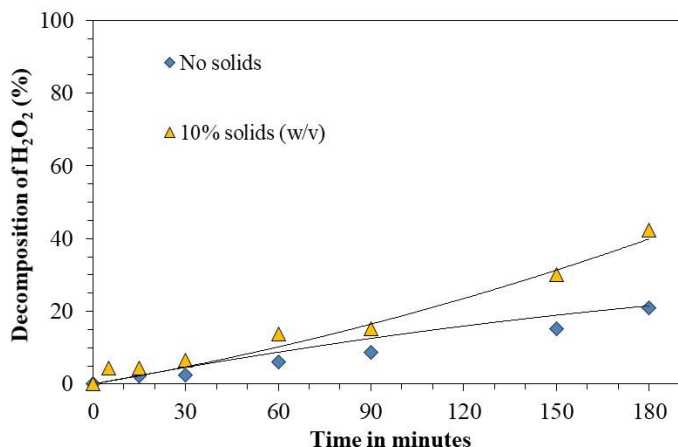


Figure 5 Effect of solids on the decomposition of H_2O_2 (%) at pH 2 and 80°C ($[\text{H}_2\text{O}_2]_0$: 0.5 M, no Cu)

Effect of addition of the polycarboxylate based solution (PBS)

The influence of a polycarboxylate based solution (PBS) as the additive on the stability of hydrogen peroxide was tested in the absence/presence of copper (5 g.l^{-1}) under different experimental conditions of pH (2-4) and temperature (20 - 80°C) (Figs. 6-8). The addition of PBS significantly prolonged the rate and extent of decomposition of hydrogen peroxide in the presence of copper (Figs. 6-7). This improvement was more apparent at low-temperature conditions (i.e. 20°C) (Fig. 6b) than at high temperatures of 50 - 80°C (Fig. 6a,c and Fig. 7a,b). To exemplify, in the presence of copper (5 g.l^{-1}) at pH 4 and 20°C , the addition of PBS at the dosage of 2.5 ml.l^{-1} led to a 56% decrease (from 73% to 17%) in consumption of hydrogen peroxide over 180 min. (Fig. 6b) while only 9% (from 99% to 90%) (Fig. 6c) and 0.4% (from 99.4% to 99.0%) (Fig. 7b) reduction in the decomposition of hydrogen peroxide was obtained at 50°C and 80°C , respectively, over the same period.

In the presence of 5 g.l^{-1} Cu at pH 2 and 50°C , increasing the dosage of PBS ($> 2.5 \text{ ml.l}^{-1}$) was sufficient for stabilisation of hydrogen peroxide (Fig. 6a) while under highly aggressive conditions (i.e. pH 4 and 80°C) even at 20 ml.l^{-1} dosage most of the peroxide (i.e. 97%) was consumed in 60 min. (Fig. 6b). At 80°C an extensive decomposition of hydrogen peroxide (by $\geq 88\%$ at 60 min.) occurred even at the highest concentration of PBS tested (20 ml.l^{-1}) (Fig. 7). It can be deduced from these results (Figs. 6-7) that under severe conditions i.e. at high levels of pH, temperature and copper, stabilising the effect of PBS on hydrogen peroxide becomes limited.

The contribution of PBS to the stability of hydrogen peroxide (Figs. 6-7) could be linked with the complexing ability of polycarboxylates with copper reducing the reactivity of copper ions [44,45]. It is pertinent to note that the addition of PBS was observed to lead to a change in the colour of the solution from blue to green, which is indicative of the formation of copper-polycarboxylate complexes. In a previous work by Bas et al. [46], the addition of PBS in cyanide leaching of a copper-rich gold ore resulted in reduced consumption of free cyanide by 39%. The authors attributed this effect to the complexation of copper with polycarboxylates, which reduces the formation of copper-cyanide complexes.

The decomposition of hydrogen peroxide was also monitored in the absence of copper at pH 2 (50 - 80°C) and pH 4 (20 - 50°C) with/without the addition of PBS (2.5 - 20 ml.l^{-1}). Hydrogen peroxide decompositions (%) was recorded to be 18.1% (pH 2, 50°C), 21.2% (pH 2, 80°C), 5.0% (pH 4, 20°C) and 16.4% (pH 4, 50°C) over the period of 180 min. in the absence of PBS (figure not shown). The

addition of PBS (2.5 - 20 ml.l^{-1}) had no effect on the stability of peroxide under the conditions tested. It can be inferred from these findings that the contribution of PBS to the stability of peroxide is essentially linked with the impediment of the catalytic effect of copper.

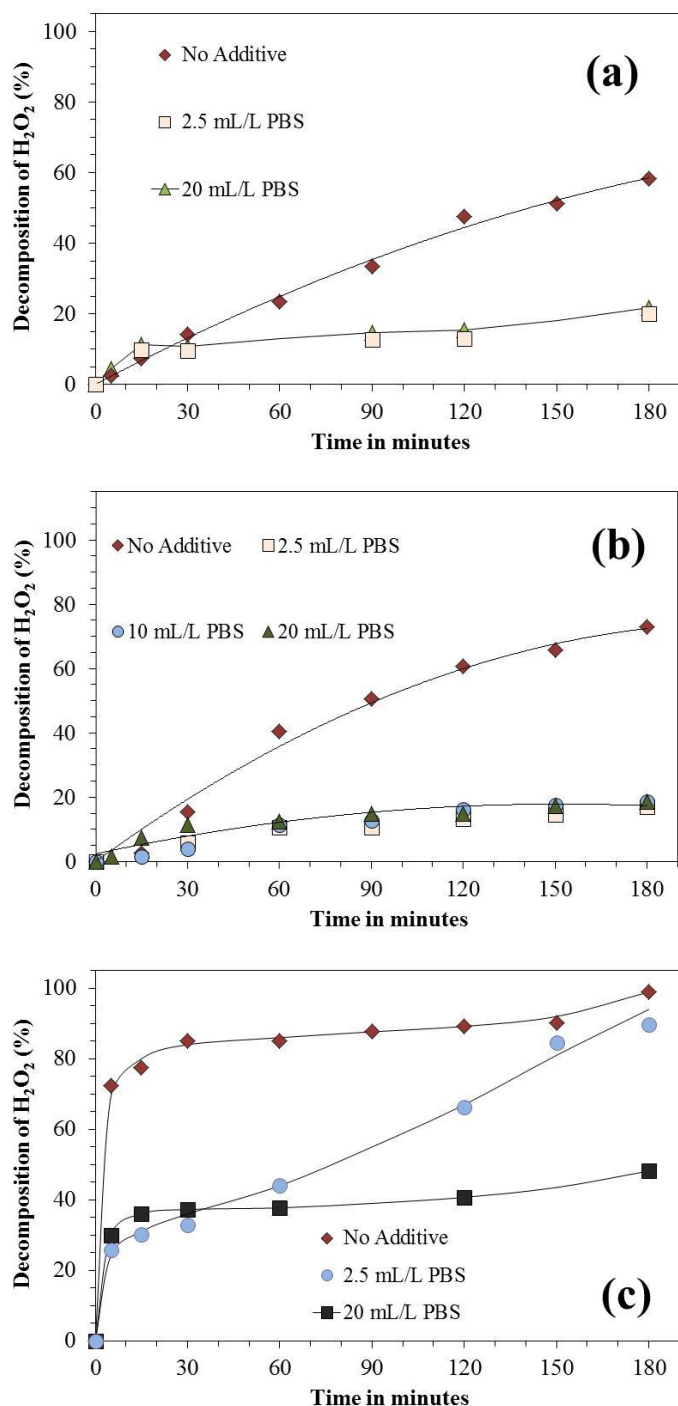


Figure 6 Effect of addition of polycarboxylate based solution (PBS) on the decomposition of H_2O_2 (%) in the presence of 5 g.l^{-1} Cu(II) at 20 - 50°C (a) pH 2, 50°C , (b) pH 4, 20°C , (c) pH 4, 50°C ($[\text{H}_2\text{O}_2]_0$: 0.5 M)

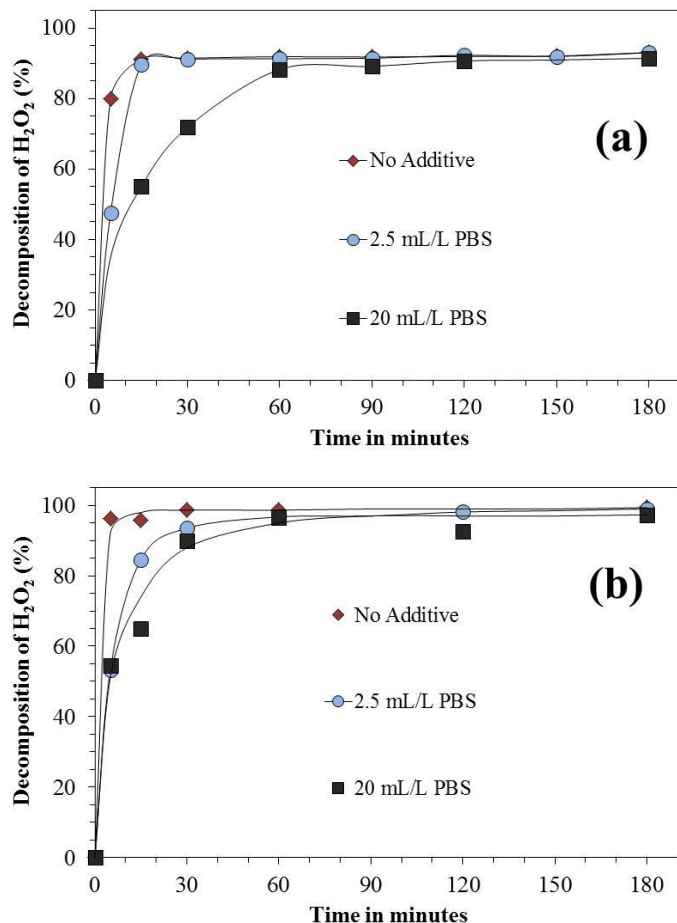


Figure 7 Effect of addition of polycarboxylate based solution (PBS) on the decomposition of H_2O_2 (%) in the presence of 5 g.l^{-1} Cu(II) at 80°C (a) pH 2, (b) pH 4 ($[\text{H}_2\text{O}_2]_0: 0.5 \text{ M}$)

Demonstration of PBS addition in hydrogen peroxide leaching of e-waste

Hydrogen peroxide can be suitably used as an oxidant for leaching of base (mainly Cu) and precious metals (Au, Ag and Pd) in sulphate/chloride media from waste electrical and electronic equipments (WEEE or e-waste) [43,47-49] in which copper content can reach up to 20% [10,50]. During leaching of e-waste, copper, as well as other metals, would dissolve and facilitate catalytic decomposition of hydrogen peroxide, which may result in low metal recoveries and high reagent consumption. Therefore, stabilisation of hydrogen peroxide is of practical importance in hydrogen peroxide leaching of e-waste.

To demonstrate the practical application of PBS for a real process, leaching tests in $\text{H}_2\text{SO}_4+\text{H}_2\text{O}_2$ solutions were performed using the waste of printed circuit boards (WPCBs) in the absence and presence of PBS (Fig. 8). Effect of PBS ($1.3\text{--}6.7 \text{ ml.l}^{-1}$) on the extraction of copper from WPCBs was tested under the conditions of $1 \text{ M H}_2\text{SO}_4$, $1 \text{ M H}_2\text{O}_2$, $\%1 \text{ w/v}$ solids at 80°C . In the absence of PBS, copper leaching was limited to $\approx 81\%$ over the period of 0.25-0.5 h (Fig. 8). The addition of PBS led to a significant improvement in extraction of copper by up to 19% i.e. from $\approx 81\%$ (no PBS) to complete extraction (6.7 ml.l^{-1} PBS) over 0.25-0.5 h. The enhancing effect of PBS on copper leaching (Fig. 8) can be essentially ascribed to the stabilisation of hydrogen peroxide through complexation of PBS with metals, copper in particular (Eqs. 2-3). Final redox potentials also indicated the contribution of PBS to stabilisation of hydrogen peroxide in that higher redox potentials were recorded in the presence of PBS i.e. 277 mV (no PBS) vs. 297 mV (1.3 ml.l^{-1} PBS) vs. 316 mV (6.7 ml.l^{-1} PBS) (Fig. 9) apparently due to the relatively high residual concentration of hydrogen peroxide in the presence of PBS. These results (Fig. 9) justify that PBS can be

suitably employed to enhance leaching of metals in hydrogen peroxide assisted lixiviant systems.

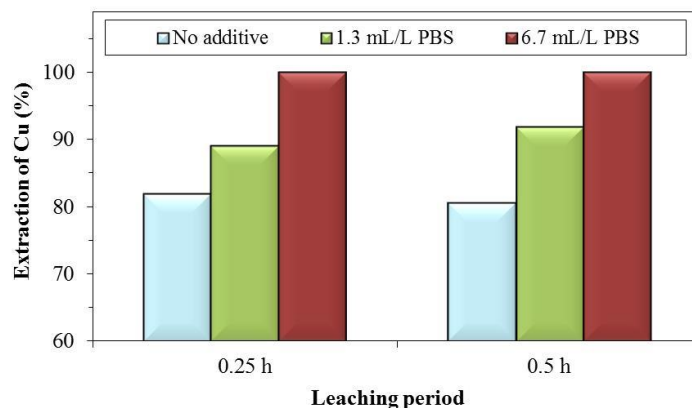


Figure 8 Effect of addition of PBS on extraction of copper from WPCBs in $\text{H}_2\text{SO}_4+\text{H}_2\text{O}_2$ solutions ($[\text{H}_2\text{SO}_4]: 1 \text{ M}$, $[\text{H}_2\text{O}_2]_0: 1$, 80°C , $\%1 \text{ w/v}$ solids)

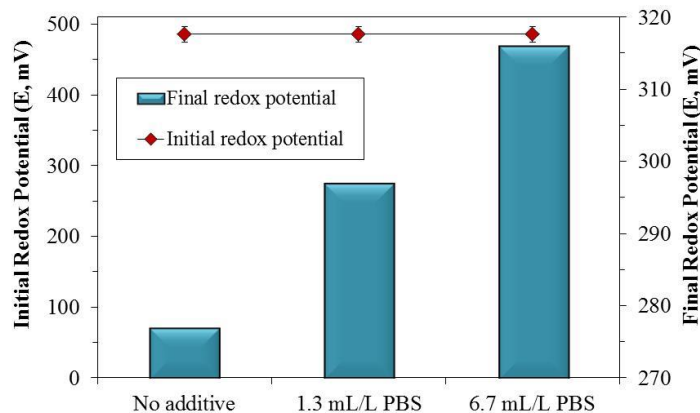


Figure 9 Initial and final redox potentials ($E_{\text{Ag}/\text{AgCl}}$, mV) in leaching of copper from WPCBs by $\text{H}_2\text{SO}_4+\text{H}_2\text{O}_2$ solutions in the absence and presence of PBS ($1.3\text{--}6.7 \text{ ml.l}^{-1}$)

CONCLUSION

Due to superior oxidising potential and its consideration as green chemical, hydrogen peroxide is extensively utilised in various industries. However, the main detraction to hydrogen peroxide is its catalytic decomposition leading to prohibitively high reagent consumption. The effect of various parameters i.e. pH (0-4), the concentration of Cu(II) (0-10 g.l^{-1}) and temperature ($20\text{--}80^\circ\text{C}$) on the rate and extent of decomposition of hydrogen peroxide was studied using design of experiments at five levels. The tests were extended to cover the effect of neutral and alkaline pH of 7.3-11.8) and solids (1-20% w/v). A commercial polycarboxylate based reagent (PBS, $2.5\text{--}20 \text{ ml.l}^{-1}$) was tested as the additive to improve stability of hydrogen peroxide in the absence/presence of copper. The results have demonstrated that decomposition of hydrogen peroxide aggravates with increasing temperature, pH and copper in descending order of significance. The calculated activation energy (E_a) of $60.7\pm 2.5 \text{ kJ.mol}^{-1}$ for decomposition of H_2O_2 indicates a chemically controlled reaction. The presence of solids was also found to adversely affect the stability of hydrogen peroxide, particularly at high temperature of 80°C . The addition of PBS was shown to significantly mitigate the catalytic decomposition of hydrogen peroxide in the presence of copper i.e. 58.3% decomposition of peroxide (no additive) compared with to 20.1% (at 2.5 ml.l^{-1} additive) in the presence of 5 g.l^{-1} Cu(II) at pH 2 and 50°C over 3 h. However, stabilising effect of PBS even at high dosages tested (20 ml.l^{-1}) was very limited at high pH and/or temperature. Contribution of PBS to the stability of H_2O_2 was observed only in the presence of copper. This was attributed to the

complexing ability of PBS with copper. The beneficial effect of PBS ($1.3\text{-}6.7\text{ ml}\cdot\text{l}^{-1}$) on H_2O_2 leaching of copper from a waste of printed circuit boards (WPCBs) was also demonstrated i.e. up to 19% improvement in leaching of copper in the presence of PBS. These findings suggest that PBS can be suitably employed to mitigate catalytic decomposition of H_2O_2 in the presence of copper in applications where it is utilised.

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