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Oxidative Degradation of phenol containing wastewater using Fenton Reagent, Permanganate and Ultraviolet Radiation

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ABSTRACT

Phenol containing wastewaters are generated by numerous industrial units including integrated steel mills, textile mills, plastic production, etc. The present work is targeted to explore the viable oxidation techniques for degradation of phenolic wastewater. Three modes of treatment have been adopted in this study, namely, sole oxidant mode using Fenton reagent or permanganate, UV-assisted oxidation and two consequent chemical oxidation steps. Results indicated the superiority of Fenton reagent over $KMnO_4$ oxidation in the sole oxidant mode. On the other hand, UV-assisted $KMnO_4$ oxidation enables almost complete COD reduction. Dual chemical oxidation mode employing $KMnO_4$ oxidation followed by Fenton reagent is also an efficient oxidative degradation system.

Key Words:* *Phenol containing wastewaters, Fenton Reagent, Permanganate Oxidation, Ultraviolet.

INTRODUCTION

Phenol is an acutely toxic chemical. It has been reported as a hazardous chemical by OSHA, EPA, ACGIA and NOISH.

In industry, wastes containing phenolic (WCPs) are encountered mainly in integrated steel mills, synthetic textile mills , manufacturing the phenolic-derived-resins (plastic industries) (1,2) , coking operations, pulp and paper operations and pharmaceutical industries.

WCPs are normally treated by lagooning, phenol extraction, thermal incineration and biological systems. Biological treatment is also applicable for degradation of phenols in wastewater under appropriate set of conditions. The trials included anaerobic and aerobic biodegradation processes for chlorophenols and cresols, utilization of a bioreactor, containing a fixed biological active biomass or employing biodegradation with immobilized large edible fungus hypha (3-6).

TREATMENT OF WCPS BY OXIDATION

Numerous methods have been explored for effective degradation of phenols. The following sections present current endeavors pertinent to phenol degradation:

a) SUPERCRITICAL WATER OXIDATION (SWO)

SWO were carried out at 315-426°C under a pressure of 24.2 MPa in a tubular reactor. Oxidation rate is influenced by temperature and concentration of water, oxygen and phenol (7,8).

b) ELECTROCHEMICAL OXIDATION (ECO)

ECO of WCPs is strongly dependent on the type of anode material used, (e.g. SnO_4 , Ti/SnO_4 or graphite) (9-11). Results indicate that the aromatic compounds with hydroxy group could be readily oxidized in the alkaline pH region (12). In the presence of NaCl, organochlorinated compounds are formed in the electrolyte which are further oxidized to volatile organics (13). Acetic and chloroacrylic acid were obtained as final products of degrading WCPs by sonoelectrochemistry (14).

c) WET AIR OXIDATION (WAO)

It depends on using oxygen as an oxidant at high temperature and pressure. The efficiencies achieved by this method are up to 99.9% (15,16).

d) CATALYTIC WET OXIDATION (CWO)

CWO of phenol using $CuSO_4$ as a catalyst in alkaline medium or using H_2O_2 in the presence of heterogeneous catalysis Fe-ZSM-5 gives the best results(17,18).

e) PHOTOCATALYTIC OXIDATION (PCO)

Ultraviolet radiation accelerates the degradation of phenols using TiO_2 as a catalyst (19,20).

f) CHEMICAL OXIDATION

Different advanced oxidation methods including O_3, H_2O_2, UV, (O_3 & H_2O_2), (O_3&UV), (H_2O_2 & UV) and (O_3 & H_2O_2 &UV), were tested in the chemical oxidation of biologically treated phenolic effluents. Oxidative degradation of WCPs using O_3 or O_3/H_2O_2 or oxygen in the presence of a catalyst comprising CuO, ZnO and gamma alumina gives good results. Using H_2O_2 in the presence of transition metals such as Fe(III) gave the optimum values at high pH(21-24).

EXPERIMENTAL INVESTIGATIONS

A. SCOPE OF WORK

The scope of this work includes oxidation of simulated phenolic wastes of 0.1%, 1% and/or 3% phenol using Fenton reagent, Potassium Permanganates and /or ultraviolet radiation. The study variables include retention time, oxidant and phenol concentrations.

B. Experimental Conditions:

Table (1) : Experimental Conditions Pertinent to Oxidation Modes

Phenol conc. Item	0.1%	1%	3%
Fenton reagent			
H_2O_2 / 50 ml sample	0.25-0.9 ml	2.5-9 ml	7.5-27 ml
Fe^{+2}/H_2O_2	1:5	1:5	1:5
Permanganate /50 ml sample	0.5-1.5 ml	5-15 ml	7.5-21.5 ml
Initial COD	6200 PPM	36400 PPM	120150 PPM
Duration	15-120 min		
Temp.	23°C		
pH ranges			
• in case of Fenton reagent	5-4		
• in case of $KMnO_4$	7, 8.6		
UV exposure time	15-120min.		

EXPERIMENTAL:

a) MATERIALS:

Chemicals utilized in oxidation experiments and its characteristics are depicted in ***table (2)***.

Table (2): Chemicals Utilized in Oxidation and its Characteristics

Materials	Characteristics	Source
Phenol	98% commercial grade	Chemicoke Egypt
$KMnO_4$		
Hydrogen peroxide	30% analar	Merk
$FeSO_4$	Powder	Merk
NaOH	Pellets	Merk
H_2SO_4	98%	Merk
COD vials	Range 0-1500 PPM	Hach

b) EXPERIMENTAL FACILITIES:

- UV Reactor, Pyrex Vessel (313nm) with high pressure lamp (Philips HPK 125w).
- Spectrophotometer HACH, DR/2000.
- Shaker Heidolph Unimax (4.5 min^{-1}).

c) OXIDATION EXPERIMENTS (METHODOLGY)

Simulated waste samples (50 ml each) of Phenol concentration 0.1, 1 and 3% are prepared.

Fenton oxidation is performed by adjusting sample pH to 3-4, followed by addition of ferrous sulfate catalyst. H_2O_2 is added slowly with gentle stirring. The reaction is terminated after the specified time by increasing pH up to 9-10. The sample is then filtered prior to COD determination.

Permanganate oxidation is undertaken by slow addition of 10% $KMnO_4$ with stirring. Reaction is terminated after the specified duration by addition of sodium bisulfite. Samples are filtered prior to COD determination.

Double oxidation mode is undertaken by $KMnO_4$ oxidation followed by pH adjusting and Fenton oxidation. Each oxidation step lasts for 30 minutes.

Ultraviolet assisted oxidation has been performed as described above for Fenton or Permanganate oxidation, in addition to post treatment by UV radiation exposure for 60 minutes.

RESULTS AND DISCUSSION:

EFFECT OF OXIDANT DOSE:

Residual COD decreases as H_2O_2 dose increases . Addition of about 7.5 ml of H_2O_2 to 50 ml of 3% phenol solution decreases COD by about 81% *Fig. (1)*.

The oxidation efficiency approaches 97% when the amount of oxidant is about 18 ml/50 ml of the phenol solution. Further addition of H_2O_2 leads to insignificant improvement. The required quantity of oxidant drops sharply with decreasing phenol concentration to 1%, since 8 ml of H_2O_2 would be required to realize COD reduction by about 98%, *Fig. (2)*. Further reduction of phenol concentration to 0.1% reduces the quantity of oxidant to 0.8 ml/50 ml to achieve 90% COD reduction, *Fig. (3)*.

Results presented in *Fig. (1-3)* and concerning phenol oxidation by 10% $KMnO_4$ solution revealed that 66.5% COD reduction could be achieved using about 21 ml of oxidant /50 ml of 3% phenol solution. It is observed that 15 ml of the oxidant is just sufficient to reduce the COD by 61%. Thus, extra 6.2 ml is needed to improve COD reduction by 5%. Reducing phenol concentration to about 1% reduces the amount of oxidant from 21 ml (in case of 3% solution) to about 10 ml of the oxidant. Thus, reducing phenol concentration by about 66% reduces the quantity of oxidant to about 50%. Further reduction of phenol concentration to 0.1% reduced the amount of oxidant to 0.5 ml and realizes higher efficiency approaching 71% which reflects the relatively higher oxidation efficiency when dealing with dilute solutions.

EFFECT OF RETENTION TIME

From the inspection of the time dependence of COD during oxidation, it is obvious that two linear rates are distinguished, *Fig. (4-6)*. The rapid COD fall zone which occurs in the first 15, 15, 30 minutes for the 3%, 1%, 0.1% phenol concentrations respectively. The second segment is characterized by highly diminished COD reduction rate. These results confirm the success of Fenton reagent to degrade phenol in wastewater. Further, the scaling up process should consider opportunities to reduce the amount of oxidant and reactor size by limiting COD reduction to acceptable limits coping with other down stream processes (e.g. biological treatment) and selection of the appropriate reaction time (e.g. 20-30 min.).

Data presented in *Fgures (4-6)* revealed the following:

- Time dependence of COD is characterized by high rate segment and other slow rate one as observed in case of Fenton oxidation.
- The time required to approach moderate degree of COD reduction, for instance 67.71%, is almost equal in the case of the 3% and 1% solution.
- On the contrary, at the same retention time (60 min) COD reduction approach 95% in case of 0.1% solution.

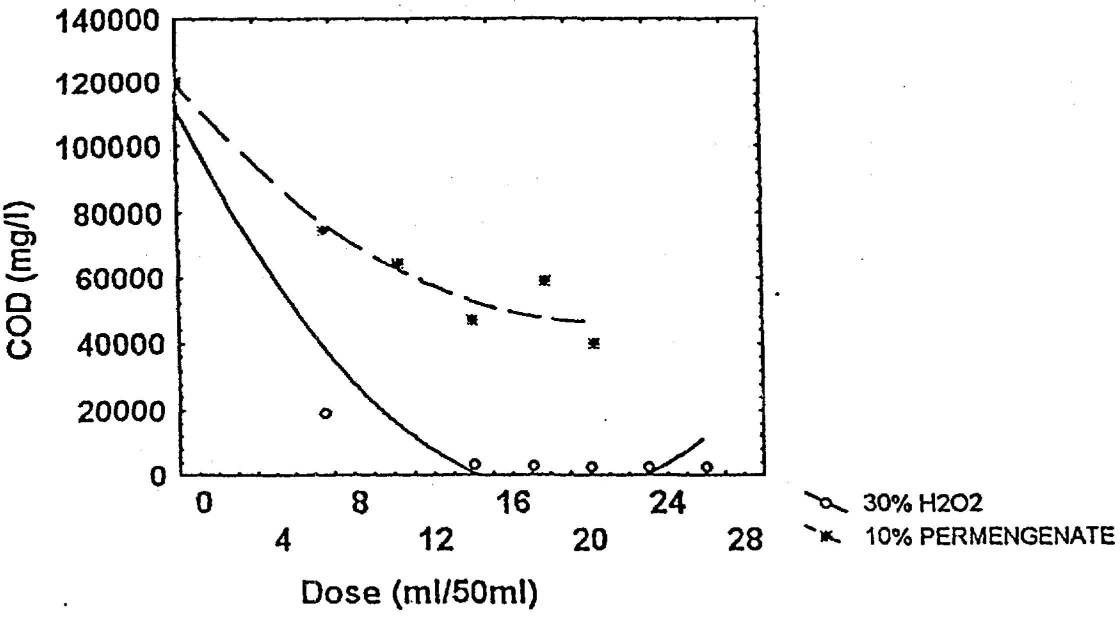

Figure (1)Effect of Oxidant Dose on Residual COD at3%Phenol

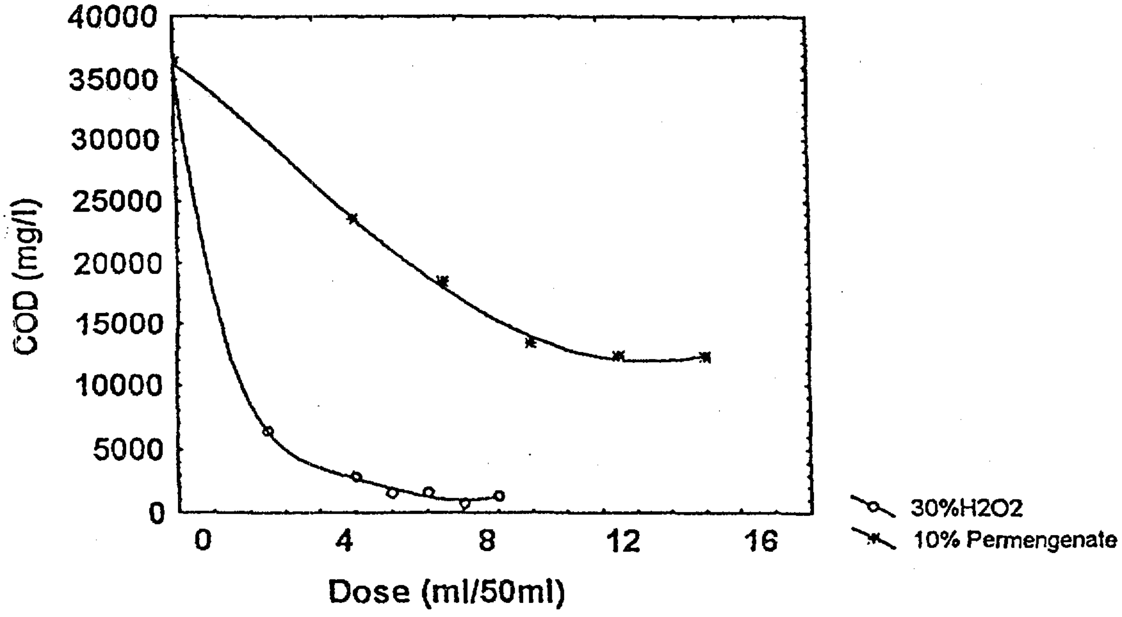

Figure (2)Effect of Oxidant Dose on Residual COD at 1%Phenol

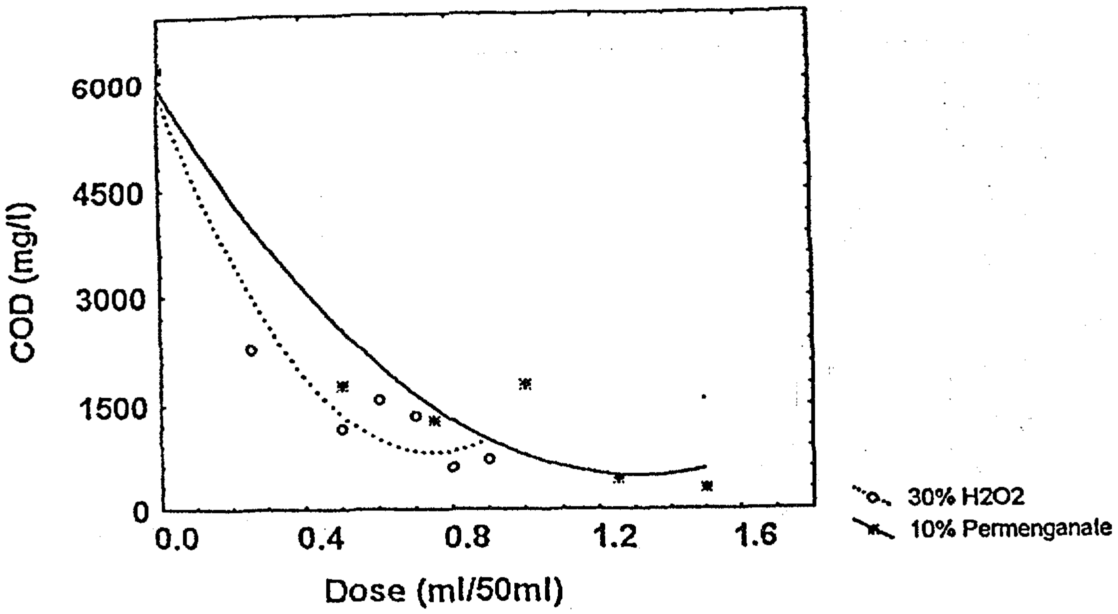

Figure (3) Effect of Oxidant Dose on Residual COD at.1%Phenol

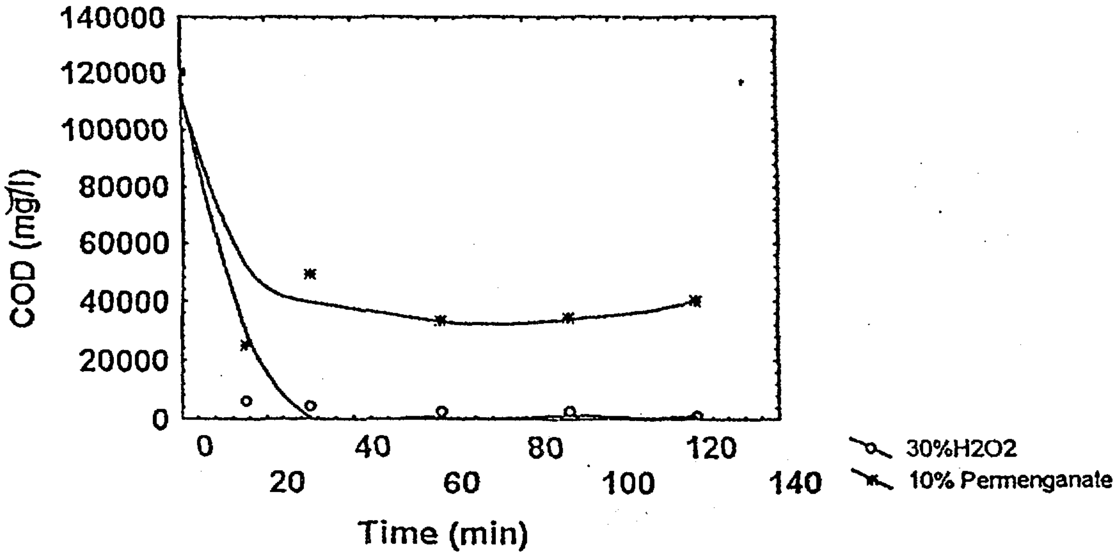

Figure (4) Time Dependance of COD Using H2O2 and Permenganate at 3% Phenol

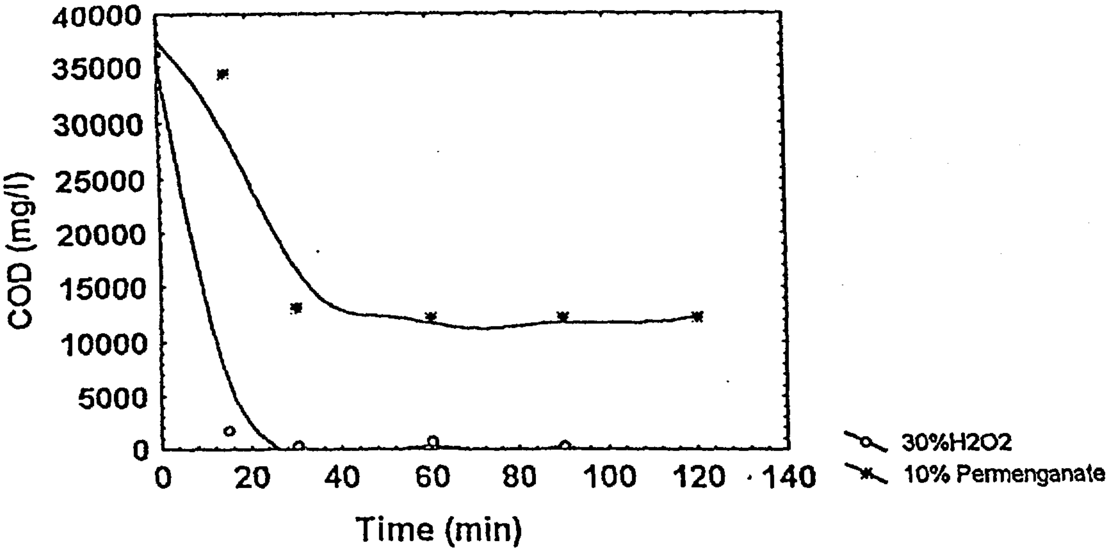

Figure (5) Time Dependance of COD Using H2O2and Permenganate at 1% Phenol

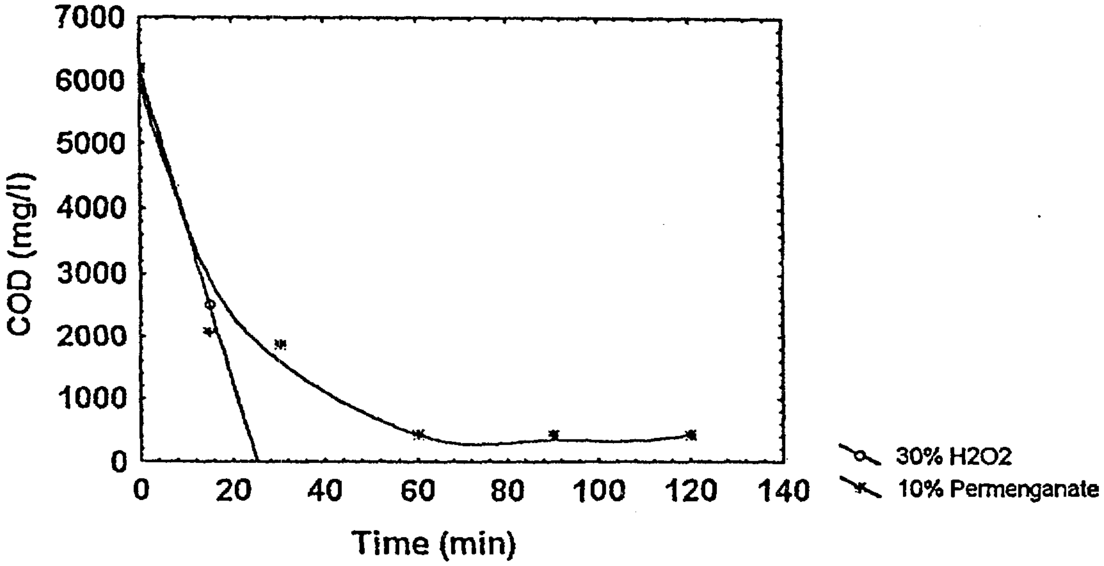

Figure (6) Time Dependance of COD Using H2O2 and Permenganate at .1%Phenol

EFFECT OF PH:

Investigations regarding the effect of pH on $KMnO_4$ oxidation (*Table 3*) confirm the tendency to realize better COD reduction at pH 7. Thus, the results described in earlier sections should manifest relatively higher values if undertaken at pH 7.

Table (3): Effect of pH on Oxidation Efficiency Using $KmnO_4$

pH	COD	Efficiency
3.5	70200	42.17
7	31400	74.17
8.6	40183	66.55

EFFECT OF ULTRAVIOLET RADIATION

The results in *Table (4)* indicate that in case of the investigated phenol concentration (0.1-3%), There is no remarkable effect of ultraviolet radiation on the oxidation of phenol using Fenton reagent. On the other hand, the ultraviolet radiation has a remarkable effect on the oxidation of phenol with $KMnO_4$, the COD has decreased from 120150 mg/l to 7500 mg/l i.e. the efficiency of phenol degradation improved from 38% to 91.8% using 3 ml of 10% $KMnO_4$ solution for 50 ml of 3% phenol concentration, while in case of using 0.2 ml oxidant/50 ml of 1% phenol solution the efficiency changed from 71 to 100%.

Effect of Double Oxidation mode

Using $KMnO_4$ treatment followed by Fenton reagent, the efficiency achieved approaches 95.2% in case of 3% phenol solution treatment efficiency approached 100% COD reduction in case of 0.1% and 1% phenol solutions.

CONCLUSION

Experimental investigation pertinent to phenol degradation by Fenton reagent, permanganate and ultraviolet revealed the superiority of Fenton reagent over Permanganate using sole oxidation mode.

On the other hand, combination of UV and $KMnO_4$ enabled almost complete COD reduction.

Numerous modes for phenol oxidation suggests adoption of Fenton reagent, $KMnO_4$ assisted UV or Fenton reagent followed by $KMnO_4$ oxidation. The choice among these modes depends on the initial phenol concentration, applicable discharge limitation and cost consideration.

Table (4): Performance of UV Efficiency

Oxidant	Fenton Reagent			$KMnO_4$		
		Performance (%)			**Performance (%)**	
Phenol Conc. (%)	**H_2O_2 Dose (ml)**	**With UV**	**Without UV**	**$KMnO_4$ Dose**	**With UV**	**Without UV**
3	3	97	93.7	3	91.8	38
3	4.5	98	97	8.5	77.28	66.55
1	2	88.2	89.6	3	60.71	50.18
1	5	94.6	90.2	6	66.5	66.11
0.1	0.2	80.9	77.4	0.2	100	70.96
0.1	0.5	90	100	0.6	100	95

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