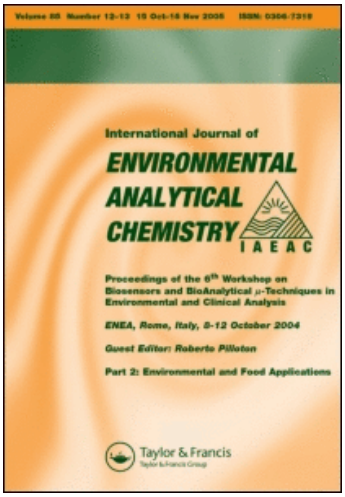

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Inhibitory Kinetic Fluorimetric Determination of Trace Phenols

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INHIBITORY KINETIC FLUORIMETRIC DETERMINATION OF TRACE PHENOLS

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An inhibitory kinetic fluorimetric method is reported for the determination of trace phenols. The proposed method is based on the inhibitory effect of phenols on the reaction of H_2O_2 oxidation of Rh6G catalyzed by Fe(III) in perchloric acid medium. The detection limit for phenol is 8.45 ng/ml. The linear range of the determination is 0.013~0.192 μg/ml. This method has been successfully used to determine phenols in crude carbolic acid, synthetic samples and industrial wastewaters. A comparison is made between the proposed and the 4-aminoantipyrine (4-AAP) methods. It is found that the method proposed in this paper is superior to the 4-AAP method.

Keywords: Kinetic fluorimetric method; phenols; Rhodamine 6G

INTRODUCTION

Phenols may occur in industrial and domestic wastewaters and in drinking water supplies. They are of significance as pollutants due to their biological effects on humans, causing dermatitis, erosion of the skin, eczema, irritation of respiratory organs and digestive disturbances. Some phenols are suspected to be carcinogenic [1,2].

The determination of phenol and its derivatives in wastewaters is therefore of great importance and many analytical methods have been developed. Chromatographic methods are suitable for the selective determination of individual phenolic compounds[3,4].

Spectrophotometric methods are frequently employed for determination of the sum of phenolic compounds. The commonly used method, i.e. the official stand-

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ard method in several countries [5–8], is based on oxidative coupling of phenol with 4-aminoantipyrine (4-AAP) in alkaline solution. The most striking deficiency of the 4-AAP method is that para-blocked phenols, such as p-cresol, do not react with the reagent. This method can be regarded only as an approximation of phenolic compounds in industrial waters and industrial wastewater. The concentration of phenolic compounds thus obtained represents the minimum amount of phenolic compounds present in the sample and, therefore, an expression of the accuracy of this method can't be made [9]. Flow-injection spectrophotometric methods have been used to determine phenols [10–12]. It is rapid, but its sensitivity is low. Some spectrophotometric methods exhibit high sensitivity, but they require extraction with organic solvent[13–16], or enrichment with membrane or resin[1,17,18]. There is always the danger of introducing contamination of the solvent [1]. Fluorescence spectrophotometric determination of phenols is rarely reported [19,20]. It can be used to determine phenolic compounds simultaneously with low sensitivity. Synchronous fluorescence spectroscopy has been employed for the determination of phenol and resorcinol in pigments [21], phenol and aniline in synthetic samples [22]. Synchronous derivative spectrofluorometry has provided the simultaneous determination of both phenol and resorcinol [23,24], phenol and o-dihydroxybenzene [25].

So far there is no report on the determination of phenols by kinetic fluorimetricphotometry. In this paper, an inhibitory kinetic fluorimetric method is proposed for the determination of trace phenols. It has been observed that phenols can inhibit sensitively the reaction of H_2O_2 oxidation of Rh6G catalyzed by Fe(III) in perchloric acid medium. The proposed method has been used to determine phenols in crude carbolic acid, synthetic samples and industrial wastewater. Compared with the 4-AAP method, there are several significant advantages by use of the proposed system to determine trace amounts of phenolic compounds. i) The system can respond to para-substituted phenols and therefore more accurate analysis are obtained when samples contain para-blocked phenols. ii) It is possible to determine accurately the concentration of phenols when samples contain cresols.

EXPERIMENTAL

Reagents and apparatus

All the reagents used in the experiment were of analytical or guaranteed grade, and redistilled water was used throughout.

Standard phenol (Phe) solution: 1.710 mg/ml (standardized with iodimetry); o-cresol (OCR) stock solution: 1.314 mg/ml; m-cresol (MCR) stock solution: 3.440 mg/ml; p-cresol (PCR) stock solution: 1.487 mg/ml; o-nitrophenol stock solution: 1.441 mg/ml; p-nitrophenol stock solution: 1.215 mg/ml; catechol stock solution: 1.246 mg/ml; resorcinol (Res) stock solution: 2.192 mg/ml; hydroquinone stock solution: 1.201 mg/ml; Rhodamine 6G (Rh6G) solution: 1.0×10^{-4} mol/l; hydrogen peroxide solution: 0.6%; perchloric acid solution: 0.1 mol/l; Fe(III) standard solution: 1.00 mg/ml. Working standard solutions were freshly prepared by appropriate dilution of the stock solutions.

Synthetic samples are made by mixing the stock solutions of different compounds. For example, in order to prepare the synthetic sample K, a certain amount of each stock solutions of phenol, o-cresol, m-cresol and p-cresol was added into a 100mL measuring flask, and diluted with water up to the mark. Then, this synthetic sample can be used for the determination.

RF-540 fluorophotometer (Shimadzu, Japan); 930 fluorophotometer (Shanghai, China); Model 501 thermostat bath (Chongqing, China).

Procedure

To a 25 ml measuring flask, add 0.40 ml of 1.0×10^{-4}mol/l rhodamine 6G, a proper amount of phenol solution, 0.70 ml of 0.1 mol/l perchloric acid, 0.70 ml of 0.6% hydrogen peroxide and 0.40 ml of 50 μg/ml Fe(III), dilute with water up to the mark before shaking. After heating in a thermostatted water bath (50±0.2°C) for 14min., the sample was cooled with running water to stop the reaction. Its fluorescence value (F) and blank value (F_0) were determined at an excitation wavelength of 348.4 nm and emission wavelength of 548.4 nm. Then the value of $\Delta F= F- F_0$ was calculated.

RESULTS AND DISCUSSION

Rhodamine 6G is a kind of triphenylmenthane dyes [26]. It emits very strong yellow-green fluorescence. When oxidized by oxidizers, its molecular structure is destroyed and the fluorescence disappears[27]. In this paper, rhodamine 6G is oxidized by hydrogen peroxide.

This reaction speeds up when Fe(III) exits in the system, indicating that Fe(III) catalyzes the reaction (Figure 1, 6–6′). When phenol is added, a complex $[Fe(OC_6H_6)_6]^{3-}$ is formed[28] and the reaction is inhibited (Figure 1, 5–5′). This shows that phenol can inhibit the oxidation of rhodamine 6G by hydrogen perox-

ide in the presence of Fe(III). Furthermore, it is observed that there is a linear relationship between ΔF and the concentration of phenol.

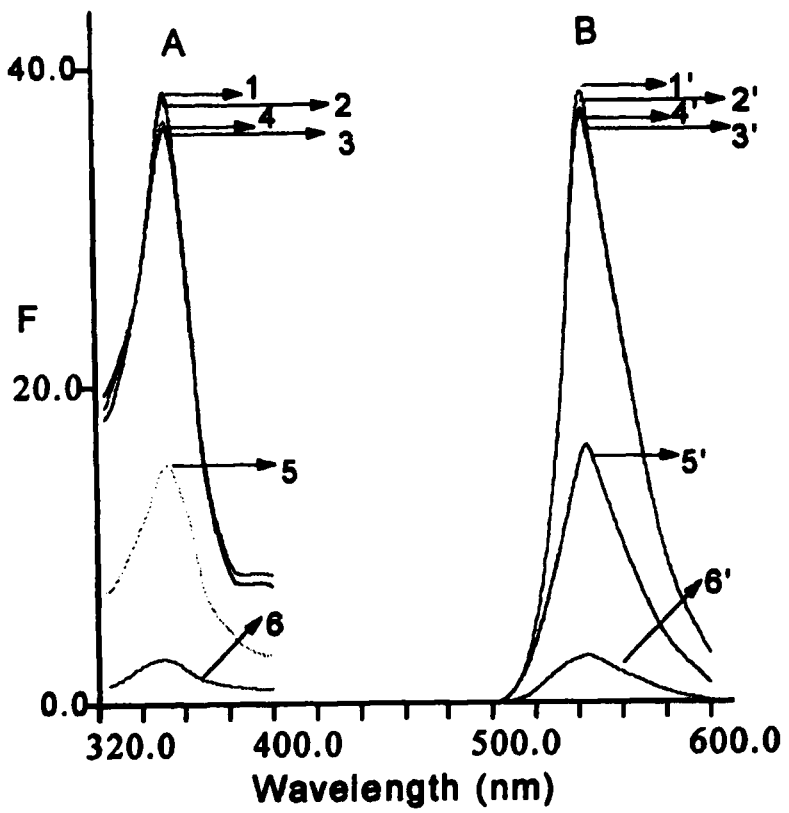

FIGURE 1 Excitation (A) and emission (B) spectra of Rh6G in the presence of different reagents. Rh6G: 1.6×10^{-6} mol/l; $HClO_4$: 2.8×10^{-3} mol/l; H_2O_2: 0.0168%; Fe(III): 0.80 μg/ml; phenol: 0.109 μg/ml; Temperature: 50.0°C; Time: 14.0 min. (1) Rh6G +$HClO_4$; (2) Rh6G +phenol; (3) Rh6G +$HClO_4$ +H_2O_2; (4) Rh6G +phenol +$HClO_4$ +H_2O_2; (5) Rh6G + phenol +$HClO_4$ +H_2O_2 + Fe(III); (6) Rh6G +$HClO_4$ +H_2O_2+ Fe(III)

Effect of variables

Various experimental parameters, including medium, reagent concentration, reaction temperature and time, were studied in order to select an optimized analytical system (with phenol concentration being 0.109 μg/ml under all conditions).

The following media have been tried in the present experiments: sulfuric acid, phosphoric acid, hydrochloric acid and perchloric acid. It was found that sensi-

tivity of the reaction is very low in sulfuric acid, phosphoric acid and hydrochloric acid. The inhibition effect of phenol is striking only in perchloric acid. The relative standard deviation (RSD) is 2.40% for 11 determinations. Therefore, perchloric acid was selected as the reaction medium.

The influence of concentrations of perchloric acid, rhodamine 6G, hydrogen peroxide and Fe(III) upon ΔF has been investigated in the range of 0.8×10^{-3}~6.4×10^{-3} mol/l, 0.8×10^{-6}~2.8×10^{-6} mol/l, 0.0072~0.0216% and 0.4~1.2 μg/ml, respectively. It is showed that ΔF value reaches a constant maximum in the range of 1.6×10^{-3}~4.0×10^{-3} mol/l perchloric acid; It decreases with increasing concentration of rhodamine 6G. The lower rhodamine 6G concentration is, the higher the detection sensitivity. However, when rhodamine 6G concentration is very low, the reproducibility is not good (RSD is 12.5% for 11 determinations); ΔF value increases with increasing concentration of hydrogen peroxide, but a large amount of hydrogen peroxide will result in bad reproducibility (RSD is 10.1% for 11 determinations); ΔF increases with Fe(III) concentration up to 0.70 μg/ml, then it remains constant. Therefore, 2.8×10^{-3} mol/l perchloric acid, 1.6×10^{-6}mol/l rhodamine 6G, 0.0168% hydrogen peroxide and 0.80 μg/ml Fe(III) were considered to be the best choice (RSD is 1.70% for 11 determinations).

The effect of reaction temperature and time were investigated in the range of 31.0~55.0 °C and 4.0~18.0 min, respectively. It was observed that the reaction rate increases with increasing temperature and reaches a maximum at 50.0°C; ΔF increases linearly with reaction time in the range of 4.0~14.0 min. Thus, 50.0°C and 14.0 min is taken as the preferable reaction temperature and time.

Analytical characteristics

The calibration graph of phenol was obtained under the optimum conditions described above. The graph is linear in the concentration range of 0.013~0.192 μg/ml. The regression equation is ΔF=0.3587+195.2C (μg/ml) with a correlation coefficient of 0.9996.

The limit of detection (taken as three times the standard deviation of the reagent blank /slope) is found to be 8.45 ng/ml. The relative standard deviation is 1.70% for 11 determinations of 0.109 μg/ml of phenol.

Interference of matrix compounds

The influence of common ions and organic compounds on the determination of 0.109 μg/ml phenol was investigated when the permitted relative deviation from

the F value is ±5%. The results are summarized in Table I. It can be seen that F^-, Cu^{2+} and NO_2^- interfere seriously in the determination. These interfering ions have been removed by distillation.

TABLE I The influence of matrix compounds

Matrix Compounds	*Ratio[a] [ion]/[phenol]*	*Matrix compounds*	*Ratio[a] [ion]/[phenol]*
NO_3^-	5.61×10^3	Mg^{2+}	7.31
K^+	3.53×10^3	Br^-	3.65
Cl^-	2.19×10^3	I^-	2.70
BrO_3^-	2.19×10^3	Cr(VI)	1.46
ClO_3^-	1.09×10^3	Hg^{2+}	2.20
Na^+	1.18×10^3	F^-	0.73
Pb^{2+}	5.85×10^2	Cu^{2+}	0.58
Cd^{2+}	2.49×10^2	NO_2^-	0.37
Se(IV)	1.46×10^2	Urea	2.01×10^3
PO_4^{3-}	1.10×10^2	Glucose	7.05×10
Ba^{2+}	7.31×10	benzoic acid	1.91×10
Mn^{2+}	3.72×10	salicylic acid	1.5
Zn^{2+}	6.01×10	p-nitrophenol	2.28
Ca^{2+}	3.29×10	hydroquinone	2.56
IO_4^-	1.83×10	catechol	0.51
Ni^{2+}	2.37×10	o-nitrophenol	1.02

a. "Ratio" stands for the ratio of concentration between the interfering substance and phenol.

Comparison of the present method with the 4-AAP method

Phenol and the related o-, m- and p-cresol isomers are toxic compounds widely used throughout industry as raw materials on an ever-expanding scale [19]. Phenols in ammoniacal liquors (wastewater) which are produced in coke and gas plants include not only phenol itself, but also its volatile homologues, notably the cresols [29]. Tables II and III give the calibration equations obtained by the present and the 4-AAP methods for the compounds chosen to represent a variety of phenolic materials. The calibration equations of cresols and resorcinol were obtained under the same conditions as phenol. It can be seen from Tables II and III that the sensitivity of the present method is higher than the 4-AAP method.

TABLE II Analytical characteristics of phenolic compounds determination by the present method (C is in μg/ml)

Phenolic compound	*Calibration equation*	*LOD*[a] *μg/ml*	*Linear range μg/ml*	R^b
Phenol	ΔF=0.3587+195.2C	8.45×10^{-3}	0.013~0.192	0.9996
o-cresol	ΔF=0.3437+205.5C	8.03×10^{-3}	0.008~0.189	0.9995
m-cresol	ΔF=-0.3210+184.4C	8.95×10^{-3}	0.011~0.192	0.9996
p-cresol	ΔF=0.1057+238.6C	6.92×10^{-3}	0.010~0.143	0.9999
resorcinol	ΔF=-0.0215+57.09C	2.89×10^{-2}	0.056~0.504	0.9994

a. Limit of detection
b. Correlation coefficient

TABLE III Analytical characteristics of phenolic compounds determination by the 4-AAP method (C is in μg/ml)

Phenolic Compound	*calibration equation*	*LOD μg/ml*	*linear range μg/ml*	*R*
Phenol	$\Delta A=-1.1628\times10^{-4}+0.2774C$	0.180	0.200~2.52	0.9999
o-cresol	$\Delta A=7.6744\times10^{-4}+0.1911C$	0.262	0.290~4.09	0.9999
m-cresol	ΔA=0.0029+0.1857C	0.269	0.310~3.77	0.9996
resorcinol	ΔA=0.0028 +0.0827C	0.604	0.400~8.46	0.9994

A comparison for the calibration curves obtained by the present and 4-AAP methods was shown in Figures 2 and 3. ΔA in Figure 3 stands for the difference in absorbance between the test and the blank solutions. It can be seen from Figure 3 that slopes of the calibration curves of phenol and other phenolic compounds are quite different by the 4-AAP method, and the slope of phenol is the largest. So determination based on the phenol calibration curve would give the minimum phenolic content of the sample [1]. Figure 2 indicates that slopes of the calibration curves of phenol and cresols are similar by the present method. So we can determine accurately the concentration of phenols expressed as phenol when there is little resorcinol in samples.

The effect of p-nitrophenol, o-nitrophenol, catechol and hydroquinone is also studied. It is observed that these compounds interfere with the reaction, but there is no linear relationship between ΔF and the concentrations of these compounds. So these compounds can not be detected by the present method. The interference effect of these compounds on the determination of phenol is also included in Table I.

Some synthetic samples are studied in order to compare the accuracy of the two methods. Table IV shows the result of a comparison study for "synthetic

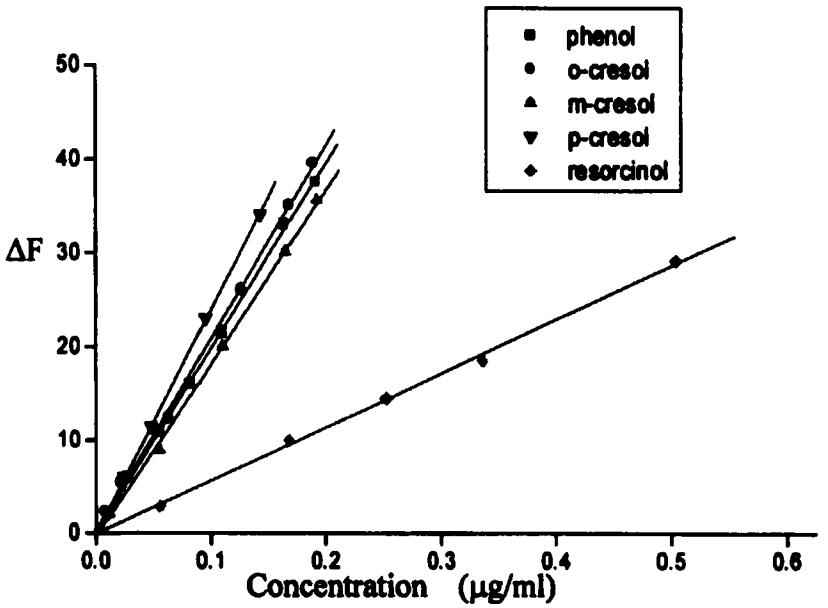

FIGURE 2 Calibration curves of phenols by the present method

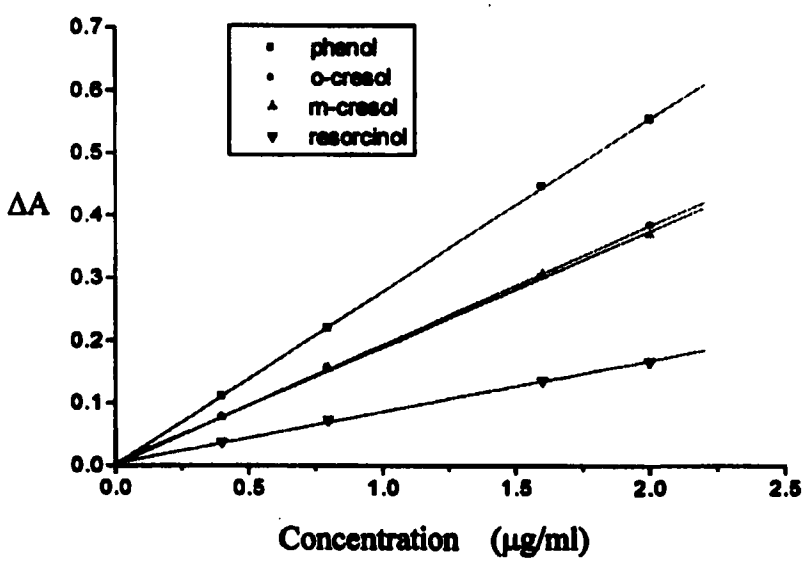

FIGURE 3 Calibration curves of phenols by the 4-AAP method

phenol" mixtures. Synthetic sample K consisted of 60% phenol, 15% o-cresol, 15% m-cresol, and 10% p-cresol. It represents a "typical" phenolic mixture. Its composition is similar to that of some real samples [9]. Therefore, this sample has been proposed [9] for the determination of phenols and used elsewhere [30]. It can be seen from Table IV that the analytical concentrations obtained by the present method for a given phenol in synthetic samples A-D, F and G are closer to the actual concentrations than those determined by the 4-AAP method. The analytical results obtained by the two methods for synthetic samples E and I are much lower than the actual concentrations. This indicated that these methods are not suitable for the determination of resorcinol in the case of phenol as standard. Synthetic samples H, K and M show that there is no reaction between 4-AAP and p-cresol. The difference in the measured total amount of phenols between the synthetic samples K and J is close to the concentration of p-cresol. Therefore, concentration of p-cresol can be determined by the present method. It can be seen from Table IV that RSD of the 4-AAP method are smaller than the present method, indicating that the precision of the 4-AAP method is better than the present method. However, the analytical concentrations obtained by the present method are closer to the actual concentrations than the 4-AAP method, suggesting that the sensitivity of the present method is higher than the 4-AAP method.

Sample analysis

The present method is used to determine phenols in real samples. A given amount of real sample is distilled as described in the literature [5]. The distillate is diluted to 250 ml in a volumetric flask. Then a known amount of this solution is used for the determination of phenols by the method proposed in this work and by the 4-AAP method. At the same time, addition recovery tests are carried out. The analytical results for some real samples are given in Table V. It can be seen from Table V that the measured concentrations obtained by the present method are generally higher than those by the 4-AAP method. This is because 4-AAP does not react with para-substituted phenols, and the slope of calibration curve of phenol is larger than other phenolic compounds in the 4-AAP method.

The industrial waste waters (1,2 and 3) listed in Table V were collected from the same chemical plant at different period of time, so were the tar waste waters (5,6 and 7) and the effluent after biochemical treatment (8 and 9). Sample 4 in Table V is crude carbolic acid, which contains relatively high amounts of cresols, so the result determined by the 4-AAP method is far lower than that by the present method. Samples 8 and 9 were collected at a spot where the biochemical dephenolization was finished. As can be seen from this table, concentration of phenols in samples 8 and 9 is so small that it can not be detected by both methods.

TABLE IV Analysis of synthetic samples by the present and 4-AAP methods[a]

Synthetic sample	*Amount added*[b] *(μg/ml)*					*Total*	*Amount found (μg/ml)*		*RSD(%) n=6*	
	Phe	*OCR*	*MCR*	*PCR*	*Res*	*amount μg/ml*	*This work*	*Official method*[c]	*This work*	*Official method*
A	6.840	–	–	–	–	6.840	6.840	6.790	2.39	0.77
B	–	10.00	–	–	–	10.00	10.45	6.919	2.90	0.18
C	–	–	10.00	–	–	10.00	9.170	6.914	3.02	1.30
D	–	–	–	10.00 –		10.00	11.66	–	3.42	–
E	–	–	–	–	10.00	10.00	1.960	2.990	4.92	6.04
F	3.420	2.628	–	–	–	6.048	6.040	5.100	2.66	1.40
G	3.420 –		3.440	–	–	6.860	6.685	5.430	4.15	1.24
H	3.420	–	–	2.974	–	6.394	6.749	3.400	4.16	0.97
I	1.094	–	–	–	2.000	3.094	1.467	1.640	4.87	1.62
J	11.89	3.022	3.096	–	–	18.01	17.06	15.50	2.71	0.82
K	11.89	3.022	3.096	1.933	–	19.94	18.98	15.50	3.18	2.42
L	4.004	2.996	3.027	–	7.979	18.01	12.52	9.699	5.22	1.60
M	4.004	2.996	3.027	2.022	7.979	20.03	14.50	9.642	3.78	1.87

[a] Results were calculated as phenol
[b] The true concentration of given compounds in the synthetic samples
[c] The 4-AAP method

TABLE V Analysis of some real samples [a]

No.		This work (μg/ml)			Official method[b] (μg/ml)
		Mean n=6	RSD (%)	Recovery (%) n=4	
1.	Industrial waste water	763.6	2.20	98.8	652.5
2.	Industrial waste water	701.9	2.36	101.0	572.9
3.	Industial waste water	843.1	3.58	95.9	593.6
4.	Crude carbolic acid	7.709×10^5	4.36	100.6	3.375×10^5
5.	Tar waste water	0.238	3.26	102.6	0.233
6.	Tar waste water	0.714	5.90	93.8	0.698
7.	Tar waste water	0.602	6.10	94.1	0.382
8.	Effluent after biochemical treatment	–	-	106.2	-
9.	Effluent after biochemical treatment	–	-	102.1	-

[a] Results were calculated as phenol
[b] The 4-AAP method

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