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Cloud Point Extraction Method for Spectrophotometric Determination of 3-Aminophenol in Environmental Samples

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Abstract: *This work describes the development of new spectrophotometric techniques for 3-aminophenol assessment. The first technique involves using benzidine in an alkaline solution to convert 3-aminophenol into a colored complex. The produced complex has a red color with an absorbance of 462 nm. Between the concentration range 5–14 μg mL^{-1}, Beer's law is obeyed with a correlation coefficient (R^2) of 0.99781, a limit of detection (LOD) of 0.0423 μg mL^{-1}, and a limit of quantification (LOQ) of 0.1411 μg mL^{-1}. The recovery was between 87.2–95.43%, the relative standard deviation (%RSD) was 2.40–3.31% and the molar absorptivity was 3.545×10^3 L mol^{-1} cm^{-1}. Secondly, cloud point extraction (CPE) was used to determine a trace amount of the colored product in the first method, followed by measuring with a UV-vis spectrophotometer. The linearity of the calibration curve was above the range of 5–14 μg mL^{-1}, and the R^2 was 0.9988. The LOD and LOQ were found to be 0.0318 and 0.1059 μg mL^{-1}, respectively. The recovery was between 99.49–99.82%, the %RSD was 0.67–2.00% and the molar absorptivity was 4.724×10^3 L mol^{-1} cm^{-1}. This method was successfully employed for 3-aminophenol detection in several wastewater samples from Rustamiya, under the Al Doura and Diyala bridge.*

Keywords: *3-aminophenol; benzidine; cloud point extraction; spectrophotometry*

■ INTRODUCTION

Water is an essential resource for life, and due to population growth, climate change, and environmental water pollution caused by sewage, industrial effluents, chemicals, domestic wastes, pesticides, pharmaceuticals, and other pollutants; access to clean and safe water has become an increasing concern around the world, particularly in developing and emerging countries [1]. Presently, just 20% of the world's wastewater is properly treated, with the vast majority being discharged into the ecosystem untreated [2-4]. Organic pollutants such as phenolic compounds, polycyclic aromatic hydrocarbons (PAHs), and chemicals used in agriculture (organic pesticides and organic herbicides) have been identified as critical issues because they cause aquatic system pollution and environmental degradation [5-6]. The presence of phenols such as 3-aminophenol in natural or drinking water is usually caused by manufacturing contamination,

and because of their severe toxicity at low concentrations, aminophenols have been designated as priority pollutants.

Several attempts have been made to remove or remediate aminophenols found in industrial wastewater [7-9]. For the selective and effective analysis of phenol in aqueous media from various types of samples, many liquid- or gas-chromatographic techniques, electrochemical techniques [10], potentiometric, spectrophotometric, spectrofluorimetric, quenched continuous fluorescence, LC-ESIMS, HPLC, and flow-injection chemiluminescent techniques have been developed [11-14]. Even though their analytical efficiency is excellent (low detection limit, high selectivity and accuracy, etc.), they are unsuitable for phenol analysis in commercial laboratories because of the high expense of analyses, multi-step and difficult sampling processes, long work times, costly tools, and so

on. Compared to these, UV-vis molecular absorption spectrometry is better suited for the development of easy, fast, and low-cost analytical methods for quantifying phenol in aqueous solutions [15-18].

One method for determining phenols and other compounds is the diazotization coupling reaction [19-20]. Diazonium salts play a crucial role as fundamental ingredients in the production of aromatic substances, pharmaceuticals, colorants, and various other organic compounds [21-23]. In optimizing conditions, cloud point extraction (CPE) has recently emerged as a promising method for the separation and pre-concentration of tiny amounts of components [24-26]. The CPE has a great importance due to its safety, speed, low cost, and high sensitivity, consequently, it has been applied as one of the evaluation and pre-concentration techniques in analytical chemistry [26-27]. CPE involves the creation of two homogenous phases, namely a water-deficient phase and an organic-enriched phase [28]. CPE relies on the phase tendencies of non-ionic surfactants when present in aqueous solutions [29-30]. Demonstrating phase segregation upon temperature elevation or introduction of a salt agent. The separation and concentration of surfactants through CPE are increasingly recognized as significant and practical applications within the realm of analytical chemistry [31-34].

In this work, the proposed technique is based totally on the azo coupling reaction of 3-aminophenol with benzidine to form a red solution, then on the estimation and pre-concentration of the usage of CPE which suggests an absorbance at 462 nm. The aim of the current study is to find the optimal conditions for estimating the 3-aminophenol in two methods. First through the azo coupling reaction with benzidin at the maximum wavelength of 462 nm and the second method is the extraction by CPE using Triton X-114 as a surfactant, and then comparing both methods.

■ EXPERIMENTAL SECTION

Materials

The reagents and ingredients used in this study were all of high quality. Distilled water was used to dissolve and prepare solutions. A stock solution of 100 μg mL^{-1} of 3-aminophenol and benzidine was prepared by dissolving 0.01 g in pure water and filling a 100 mL volumetric flask to the mark with distilled water. A 1% sodium nitrite (NaNO$_2$) solution was made by dissolving 1 g of NaNO$_2$ in distilled water and completing the mark in a 100 mL volumetric flask, and a 1% urea solution was made by dissolving 1 g of urea in 100 mL of distilled water, 1 M of H$_3$PO$_4$, H$_2$SO$_4$, HCl, and CH$_3$COOH and 1 M of NaOH, NaHCO$_3$, KOH, and Ba(OH)$_2$ were prepared by dissolving an appropriate amount in distilled water. Then, 10% (v/v) of each Triton X-100, Triton X-114, and Tween 20 was prepared by dissolving 10 mL in distilled water and completing the mark in a 100 mL volumetric flask.

Instrumentation

Sensitive electric balance (Sartorius, Germany), bench centrifuge (type MSE manufacture, England), a thermostatic water bath (Germany), and UV-vis spectrophotometer (a Shimadzu Model 160A, Japan, with a response time of 0.1 s) were employed for spectrophotometric analysis. A quartz cell with a 1 mL internal volume and a 1 cm route length was used to test absorbance.

Procedure

General azo coupling procedure

The prepared azo coupling product is added in a volumetric flask 10 mL in an ice bath, followed by adding 1.0 mL of benzidine, 1.0 mL of HCl, 1.0 mL of NaNO$_2$, 1.0 mL of urea, 1.0 mL of 3-aminophenol, and 1.0 mL of NaOH. The absorption is then determined using UV-vis. The spectra of maximum wavelength absorption are measured.

General CPE procedure

The CPE test involves multiple steps. First, a series of 10 mL volumetric flasks is filled with the optimal volumes that were previously determined, which were 0.6 mL benzidine, 0.8 mL CH$_3$COOH, 1 mL NaNO$_2$, 0.8 mL urea, 1.0 mL 3-aminophenol, 1.0 mL NaOH, and 1.0 mL 10% (v/v) Triton X114. Then, complete the volume with distilled water. The volumetric contents were transferred to a centrifuge test tube, and the

mixture was placed in a bath of water at 60 °C for 20 min before being centrifuged at 4,000 rpm for 20 min. The micelles split easily after 1 min of increasing viscosity in an ice bath. The sediments were dissolved in 3 mL of ethanol, and an UV-vis was used to measure the absorbance.

Recommended procedure for environmental water samples

The wastewater samples were collected from various locations including tap water, Rustamiya, under Al Doura and Diyala bridges, and then kept in plastic bottles before being filtered with filter papers. First, 10.20 μg mL^{-1} of 3-aminophenol was prepared in 100 mL volumetric flask, 1.2 mL from 100 μg mL^{-1} of 3-aminophenol was taken and diluted the volume with distilled water. Then, in a series of 10 mL volumetric flasks, the optimal volumes were added 0.6 mL benzidine, 0.8 mL CH_3COOH, 1.0 mL $NaNO_2$, 0.8 mL urea, 10.20 μg mL^{-1} of 3-aminophenol, 1.0 mL NaOH, and complete the volume with distilled water. The absorption was measured with a spectrophotometer, then the same procedure followed but with wastewater and the absorbance was measured. After that, the absorbance was measured with CPE technique by adding all optimal volumes in a series of 10 mL volumetric flask of 0.6 mL benzidine, 0.8 mL CH_3COOH, 1.0 mL $NaNO_2$, 0.8 mL urea, 10.20 μg mL^{-1} of 3-aminophenol, 1.0 mL NaOH, 10% (v/v) triton X-114

and completed the volume with wastewater.

■ RESULTS AND DISCUSSION

Absorption Spectra

This research reported the diazotization of benzidine and its coupling with 3-aminophenol to form a red color mixture at 462 nm. Fig. 1 depicts the spectrum of absorption of red color versus a blank.

The Optimization of Diazonium Salt Reaction Analysis

Various factors influenced the absorption of colored azo products, including acid type and volume, sodium nitrite volume, reagent volume, and NaOH volume. The effect of several acids (1 M) on the production of diazonium salt was investigated and the results are shown in Fig. 2(a). The best acid is CH_3COOH and the best volume of 1 M CH_3COOH was 0.8 mL, as shown in Fig. 2(b). The optimal acid volume is then determined in the following analysis.

The influence of various bases on the synthesis of the azo compound 1 M of KOH, NaOH, $Ba(OH)_2$, and $NaHCO_3$ was studied. The results show that NaOH was the best base, as shown in Fig. 3(a). The best absorbance value was obtained by adding 1 mL of NaOH, as shown in Fig. 3(b). In the following analysis, the optimal volume of base is used in the next analysis.
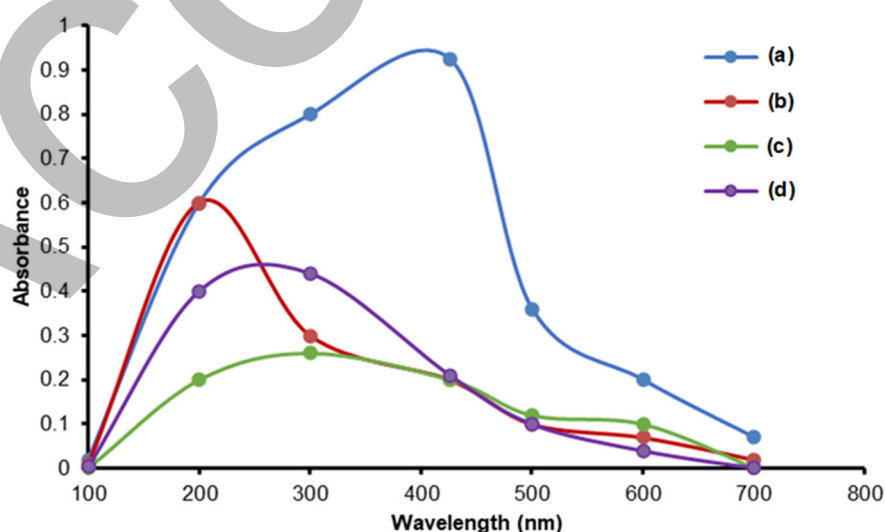

Fig 1. (a) Absorption of the resulting dye's spectra of 3-aminophenol versus blank, (b) 3-aminophenol versus the ethanol, (c) the reagent benzidine versus ethanol, and (d) the blank versus distilled water
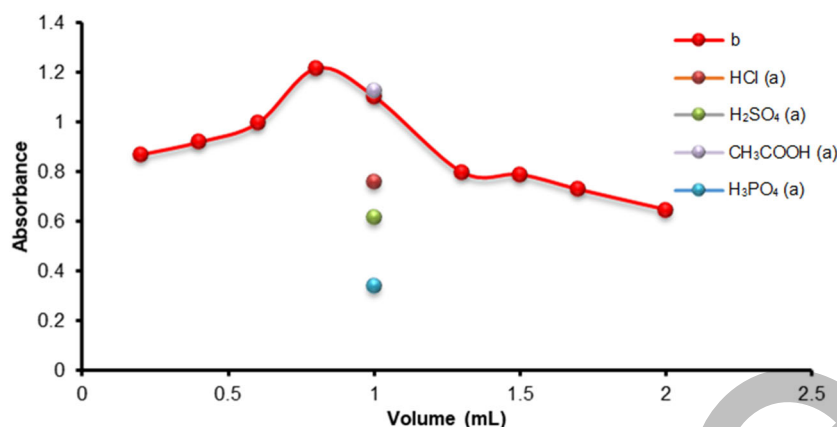
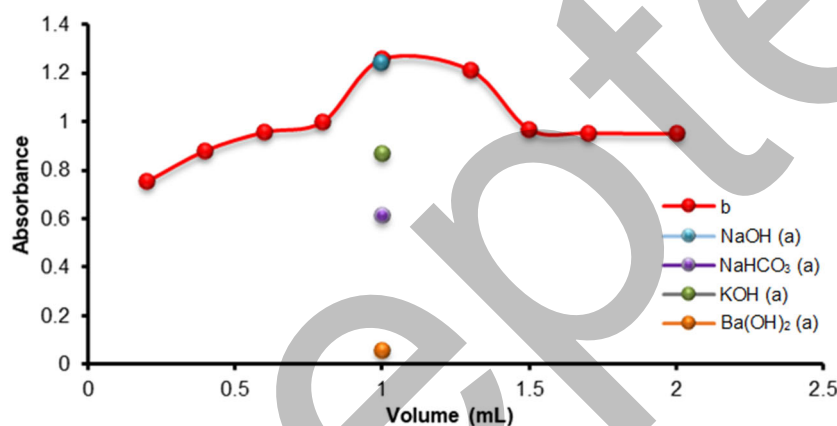**Fig 2.** Effect of (a) acid type and (b) acid volume on the absorbance value

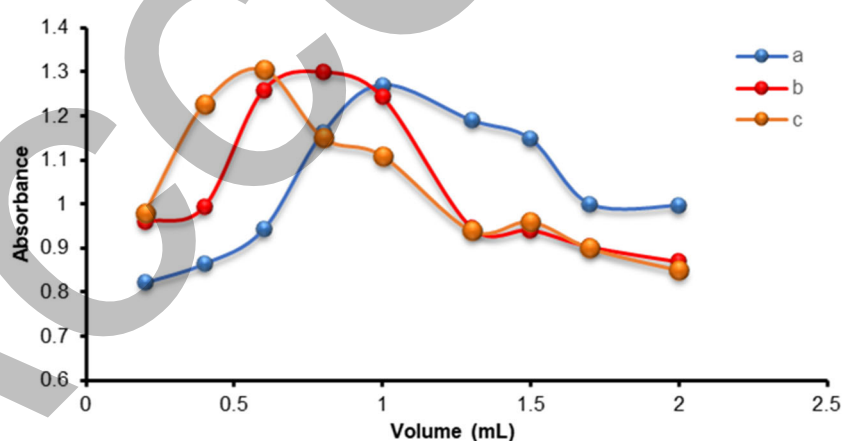**Fig 3.** Effect of (a) base type and (b) base volume on the absorbance value

Fig 4. Effect of (a) $NaNO_2$ volume, (b) urea volume, and (c) benzidine volume on the absorbance value

The effect of $NaNO_2$ concentrations was investigated by varying the volumes of $NaNO_2$ solution used in the diazotization method from 0.2 to 2.0 mL and discovering that 1 mL provided the best absorption, as shown in Fig. 4(a). In the following analysis, the optimum volume of $NaNO_2$ is used in the next analysis. To empty out the excess $NaNO_2$, a range of 1% urea volumes ranging from 0.2 to 2.0 mL were used, as shown in Fig. 4(b). Urea (1 mL) was sufficient to remove the remaining amount. The optimal urea volume is then determined in the

following analysis. According to Fig. 4(c), 0.6 mL of benzidine reagent was used to achieve a high absorbance at λ_{max} 462 nm.

To determine the stoichiometry of the 3-aminophenol ratio, the mol ratio method was used by preparing a series of different volumes from 0.1 to 3.5 mL from 3×10^{-4} µg mL^{-1} benzidine, with 1 mL of 3×10^{-4} µg mL^{-1} 3-aminophenol under optimal conditions of 0.6 mL benzidine, 0.8 mL CH$_3$COOH, 1 mL NaNO$_2$, 0.8 mL urea, and 1 mL NaOH. The stoichiometric ratio between reagent (R) and phenol (PH) results in 1:1 as shown in Fig. 5(a), and the continuous variation method (Job's method) was used by preparing a series of different volumes of 0.1–0.9 mL of each reagent and phenol under optimal conditions of 0.6 mL benzidine, 0.8 mL CH$_3$COOH, 1 mL NaNO$_2$, 0.8 mL urea, and 1 mL NaOH. The results showed that the ratio of 3-aminophenol to reagent is 1:1 as shown in Fig. 5(b).

The Calibration Curve

By adding 0.6 mL benzidine, 0.8 mL CH$_3$COOH, 1.0 mL NaNO$_2$, 0.8 mL urea, 5–14 µg mL^{-1} 3-aminophenol, and 1.0 mL NaOH to several sets of 10 mL volumetric flasks set in an ice bath; a small amount of 10 mL solution with an increasing concentration of 3-amino phenol is prepared. The phenol is then measured spectrophotometrically at its maximum wavelength, as shown in Table 1 and Fig. 6. The results show the precision and accuracy of the proposed method for determining complex standards. The confidence limit (C.L) for the concentration (µg mL^{-1}) [28] has been calculated from the following Eq. (1) [24];

$$C.L = \overline{X} \pm t\left(\frac{S}{(n)^{1/2}}\right) \qquad (1)$$

where S = standard deviation, n = the number of samples (number degrees of freedom), $\overline{X}$ = rate of measurements (concentration or absorbance), t = test-t at (n-1) from degrees of freedom at C.L 99%. Ten replications are studied for blank solution in order to calculate LOD and LOQ as shown in the following Eq. (2) and (3), respectively.
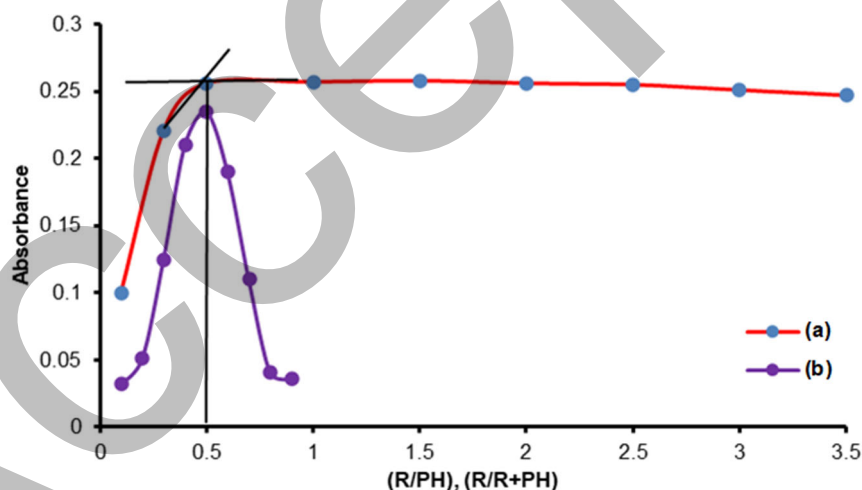

Fig 5. (a) The mole ratio method and (b) for continuous variation method of 3-aminophenol

Table 1. Precision and accuracy of the proposed method for the determination of standard of complex (n=5)

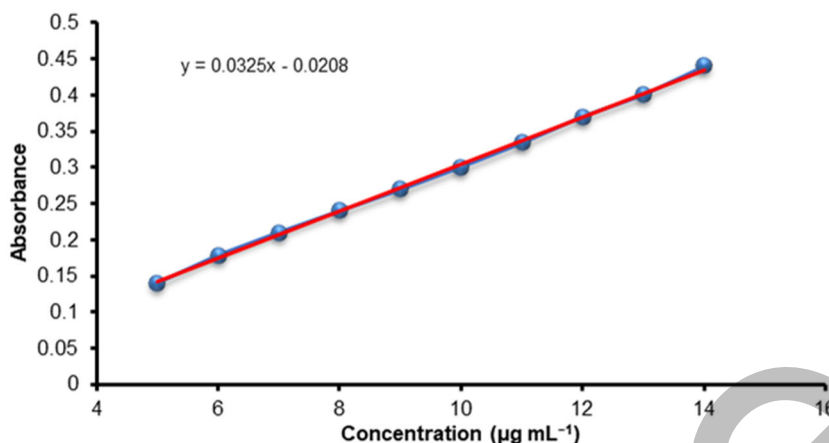| Amount taken (µg mL^{-1})	Amount found (µg mL^{-1}) (mean ± SD)	C.L at 95%	%Rec	%E$_{rel}$	%RSD
5	4.36 ± 0.0049	4.36 ± 0.0061	87.20	-12.80	3.31
7	6.36 ± 0.0071	6.36 ± 0.0088	90.85	-9.14	3.20
10	9.36 ± 0.0083	9.36 ± 0.0103	93.60	-6.40	2.60
12	11.36 ± 0.005	11.36 ± 0.0062	94.66	-5.30	1.31
14	13.36 ± 0.012	13.36 ± 0.0139	95.43	-4.57	2.40

Fig 6. Calibration curve of 3-aminophenol

$$LOD = \frac{SD X 3}{S} \quad (2)$$

$$LOQ = \frac{SD X 10}{S} \quad (3)$$

The special relationship to calculate the %RSD, the relative error percentage (%E_{rel}), and the recovery percentage (%Rec) were calculated using Eq. (4-6), respectively;

$$\%RSD = \frac{S}{\overline{X}} \times 100 \quad (4)$$

where, S = standard deviation and $\overline{X}$ = the arithmetic mean of the measurements;

$$\%E_{rel} = \frac{(Found - Taken)}{Taken} \times 100 \quad (5)$$

where, Found = analytical result of the concentration and Taken = the real result of the concentration.

$$\%Rec = \%E_{rel} + 100 \quad (6)$$

Surfactant Type Effect

Because each surface has spectral characteristics that are determined by the practical basis of micelles, the type of surfactant used is critical in the CPE procedure. The CPE method was used by adding a series of different volumes prepared from 0.2 to 2 mL in 10 mL volumetric flask solutions containing optimal volumes of 0.6 mL benzidine, 0.8 mL CH_3COOH, 1 mL $NaNO_2$, 0.8 mL urea, 1 mL 3-aminophenol, 1 mL NaOH, and 10% (v/v) Triton X-114, and completed the volume with distilled water, then are mixed, heated at 60 °C for 20 min to form cloud point, then centrifugate at 4,000 rpm for 20 min, separating the surfactant-rich phase, and dissolved it in

3 mL ethanol and measure at λ_{max} 462 nm. The best volume of surfactant is 1.3 mL as shown in Fig. 7.

The two conditions to improve effective phenol extraction and pre-concentration, equilibrium temperature and time incubation, were deemed necessary steps to complete the CPE. Temperatures ranged from 30 to 65 °C, with incubation times ranging from 5 to 35 min. In the following steps, an equilibration temperature of 55 °C and a time limit of 20 min were chosen, and the sample was centrifuged for 20 min at 4,000 rpm before cooling for 1 min, resulting in a high recovery of phenol in a short period of time. After the extraction procedure of CPE was completed, the aqueous solution was decanted, and ethanol was added to reduce the viscosity of the surfactant-rich phase and facilitate its transfer into a spectrophotometric cell. After all, 3 mL of ethanol was used in the following experiment.
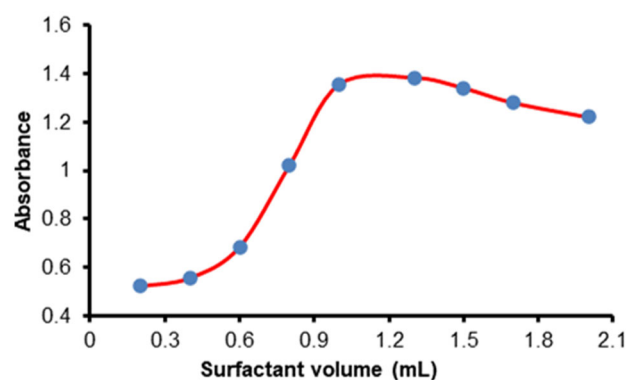

Fig 7. Correlation curve of absorbance versus volume of Triton X-114 for 3-aminophenol

Calibration Curve for CPE

To evaluate 3-aminophenol, the CPE technique's optimized parameters were used. A calibration curve was created by plotting the 3-aminophenol concentration of 5–14 µg mL^{-1} versus absorbance, as shown in Fig. 8. The analytical parameters with and without a cloud point are listed in Table 2. Table 2 shows that the technique of extracting at the cloud point, which has high enrichment and pre-concentration factors, is a great novelty for extracting small amounts of 3-aminophenol. Table 3 shows the precision and accuracy of the proposed method for determining complex standards by cloud point.

The C.L for slope and intercept has been calculated from the following Eq. (7) and (8) [31];

$$C.L = b \pm tSb \qquad (7)$$
$$C.L = a \pm tSa \qquad (8)$$

when C.L is confidence limit, b and a are the slope and intercept, respectively, at C.L 99% (n-2), $S_{y/x}$ is standard deviation of change y value, Sb is standard deviation of slope (b), and Sa is standard deviation of intercept (a).

Application of Real Samples

The method that was created is used to determine 3-aminophenol in an aqueous environment. Different 10.20 µg mL^{-1} of 3-aminophenol samples are taken and the proposed method is applied, and then the concentrations are extracted from the regression line
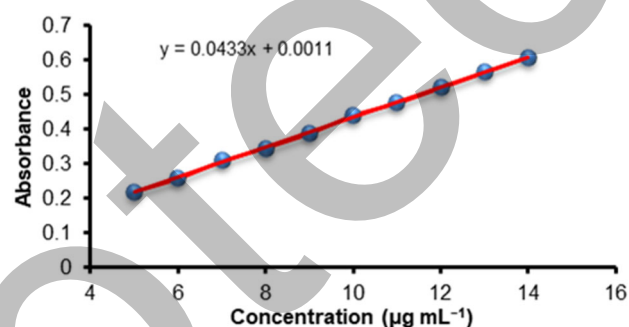

Fig 8. Calibration curve of CPE of 3-aminophenol

Table 2. Analytical parameter of CPE method

Type of parameter	Before CPE	After CPE
Color	red	red
Wavelength λ $_{max}$ (nm)	462	462
Concentration range (µg mL^{-1})	5-14	5-14
Regression equation (y)	y = 0.0325x - 0.0208	y = 0.0433x + 0.0011
R	0.9989	0.9994
R^2	0.9978	0.9988
LOD (µg mL^{-1})	0.0423	0.0318
LOQ (µg mL^{-1})	0.1411	0.1059
Sandell's sensitivity (µg cm^{-2})	0.0308	0.0231
Slope (m)	0.0325	0.0433
Intercept (C)	0.0208	0.0011
Standard error for regression line (S$_{y/x}$)	0.0035	0.0044
Sa	0.3088	0.3967
Sb	0.000377	0.00049
C.L for slope (b ± tSb) at 95%	0.0325 ± 0.0009	0.0433 ± 0.00112
C.L for intercept (a ± tSa) at 95 %	0.0208 ± 0.71199	0.0011 ± 0.9146
C.L for 5 µg mL^{-1} at 95%	4.36 ± 0.0061	4.98 ± 0.00557
C.L for 7 µg mL^{-1} at 95%	6.36 ± 0.0088	6.98 ± 0.00652
C.L for 10 µg mL^{-1} at 95%	9.36 ± 0.0103	9.98 ± 0.0067
C.L for 12 µg mL^{-1} at 95%	11.36 ± 0.0062	11.98 ± 0.00362
C.L for 14 µg mL^{-1} at 95%	13.36 ± 0.0139	13.98 ± 0.0051
Molar absorptivity (L mol^{-1} cm^{-1})	3.545 × 10^3	4.724 × 10^3
Composition of product	1:1	1:1
Preconcentration factor (Enrichment factor) % [35]	-	133.3%

Table 3. Precision and accuracy of the proposed method for the determination of standard of complex (n = 5) by cloud point

Amount taken (µg mL^{-1})	Amount found (µg mL^{-1}) (±SD)	C.L at 95% (mean ± SD)	%Rec	%E$_{rel}$	%RSD
5	4.98 ± 0.0045	4.98 ± 0.0056	99.49	−0.51	2.00
7	6.98 ± 0.0042	6.98 ± 0.0066	99.64	−0.37	1.60
10	9.98 ± 0.0055	9.98 ± 0.0068	99.75	−0.26	1.20
12	11.98 ± 0.0029	11.98 ± 0.0037	99.79	−0.22	0.56
14	13.98 ± 0.0041	13.98 ± 0.0051	99.82	−0.19	0.67

Table 4. Application of the proposed CPE for the evaluation of 3-aminophenol

		Before CPE					
Water source	Phenol conc. (µg mL^{-1})	Found	%Rec	Average %Rec	%E$_{rel}$	Average %E$_{rel}$	%RSD
Tap water	10, 20	9.87, 19.87	98.7, 99.4	99.02	−1.30, −0.65	−0.97	0.85, 0.63
Rustamiya	10, 20	9.63, 19.63	96.3, 98.1	95.50	−5.97, −2.99	−4.47	2.98, 0.23
Under Al doura bridge	10, 20	9.60, 19.60	96.3, 98.15	97.20	−3.60, −1.84	−2.77	1.14, 0.96
Diyala bridge	10, 20	9.94, 19.94	99.41, 99.7	99.56	−0.58, −0.29	−0.43	0.85, 0.84
		After CPE					
Water source	Phenol conc. (µg mL^{-1})	Found	%Rec	Average %Rec	%E$_{rel}$	Average %E$_{rel}$	%RSD
Tap water	10, 20	9.99, 19.99	99.95, 99.98	99.97	−0.05, −0.03	−0.04	1.26, 0.45
Rustamiya	10, 20	9.50, 19.50	95.70, 97.80	96.68	−4.42, −2.21	−3.31	0.34, 0.13
Under Al doura bridge	10, 20	9.89, 19.89	98.96, 99.48	99.23	−1.03, −0.51	−0.77	0.86, 0.55
Diyala bridge	10, 20	9.77, 19.77	97.70, 98.90	98.30	−1.66, −1.73	−1.70	0.91, 0.34

Table 5. Comparison between the present method and other methods for aminophenol

Analytical method	Color	Wavelength (nm)	Linear range (µmol L^{-1})	%Rec	LOD (µmol L^{-1})	%RSD	Ref.
CPE method	red	462	5–14	99.7	0.0318	1.206	This study
Copper nanowires/poly(naphtoquinone chromium (III))	-	-	1.0–5.5	-	0.20	-	[36]
Semi-quantitative detection with colorfully naked-eye assay	red	776	0.5–20.0	-	0.27	-	[37]
Selective and sensitive colorimetric detection	-	-	0–85	94.0	0.32	-	[38]
Simultaneous determination of aminophenol isomers	-	-	0.3–18	98.7–104.6	0.05	0.999	[39]

equation of the calibration curve. The results before and after using the CPE technique are shown in Table 4.

Comparing the Suggested Method with Other Methods

The comparison between suggested methods and other methods is shown in Table 5, which explains the results of CPE and other methods. It is clear that the CPE method gives a good %RSD and a low LOD and has a wide linear range compared with other methods.

■ CONCLUSION

A simple, fast, and spectrophotometric technique for estimating small amounts of 3-aminophenol with

benzidine as a reagent has been developed. The first method involved converting phenol to azo pigment, which was then spectrophotometrically measured at λ_{max} 462 nm. The second method uses CPE to determine and pre-concentrate 3-aminophenol with Triton X-114 as a surfactant to reduce surface tension. The proposed method was found to be effective and recoverable, and it was applied to several water sources from different regions. The method is cheap, and it has less consulting time compared with the other methods like SPE, liquid-liquid extraction, and HPLC. It was discovered by comparing it to other methods in the literature, and CPE was found to be the best method for simplifying the application. CPE gives a good %RSD and a low LOD and has a wide linear range.

■ ACKNOWLEDGMENTS

■ CONFLICT OF INTEREST

The authors declare no conflicts of interest. We confirm that all the Figures and Tables in the manuscript belong to us.

■ AUTHOR CONTRIBUTIONS

Alaa Mousa Imran conducted and carried out the experiments, data acquisition, analysis, and interpretation, and participated in drafting the manuscript. Saadiyah Ahmed Dhahir and Ahmed Jassim Muklive help in interpretation, analysis, and conceptualization of the manuscripts. All authors read and reviewed the final manuscript.

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