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Competence azo dyes sensors of new based fluorophores for spectrophotometric trace determination of cobalt in real water samples

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ABSTRACT

In this work, a simple, time saving, accurate and sensitive method for the direct spectrophotometric detection of cobalt ion using two new fluorophore azo dyes, R1 and R2, were achieved. The method based on a complex formation between Co(II) and these two azo compounds-based fluorene and pyrene moieties. To attain the optimal conditions for the detection of cobalt ion, several parameters such as effect of solvents, pH, reagent concentration, sequence of addition, temperature and time were explored. The absorption maximum for Co(II)-R1 and Co(II)-R1 orange color complexes was accomplished at 472 nm using pH 8.97 of universal buffer and 470 nm using pH 10.98, respectively. The calibration graphs were linear over the concentration range of 0.2–3 and 0.4–3 μ g mL⁻¹ of Co(II) for Co(II)-R1 and Co(II)-R1, respectively with a stoichiometric ratio of (1:2) (Co²⁺: reagent). Various statistical analytical parameters including molar absorptivity, limit of detection, limit of quantification, precision and accuracy were estimated. In addition, the established approach was efficiently exploited for Co(II) determination in some water samples. The findings of this investigation may pave the way for advancements in sensor technologies.

1. Introduction

Azo dyes are known as organic-colored compounds which contain the azo group (Ar–N = N–Ar) in the structure, and it is considered as the most diverse group (Benkhaya et al., 2020). Generally, the azo dyesbased compounds, the azo group is coupled with two mono or polycyclic aromatic systems (Hashemi Kaykhaii 2022). Due to the physicochemical and biological qualities of azo compounds, a wide range of applications including pharmaceutical, cosmetic, food, dyeing/textile, corrosion inhibitors, and analytical chemistry industries use these dyes (Ali et al., 2018, Aljamali Hassen 2021). In addition, azo dyes have a huge number of biological activities which was previously reported for its pharmaceutical importance as antibiotic, antifungal, and anti-HIV (Ali et al., 2019, Weglarz-Tomczak and Górecki, 2012). Azo dyes are also used in analytical assays such as spectrophotometer techniques (Abdallah, 2012, Hulanicki and Głąb 1978, Nguyen and Saleh, 2016). The presence of azo group (R-N = N-R) led to shift their absorption maxima bathochrmically and absorbed in the visible light due to the chromophoric characteristic of this dye class.

Substances such as heavy metals, organic amines, inorganic

pollutants and nitrophenol have the potential to contaminate the environment. Therefore, several methods have been proposed for the determination of these harmful compounds (Liu et al., 2020, Pan et al., 2023, Zhang et al., 2024, Zhong et al., 2024). Cobalt is one of the natural earth elements that exist in trace amount in the earth's environment. It has been applied for several purposes such as pigments, glass, metal alloys and as catalysts for petroleum industries (Kazi et al., 2012). It also exists in the chemical structure of vitamin B12, some enzymes, and it is well known to be an essential micronutrient in animals and plants for metabolic processes (Santos et al., 2020). However, one of the major issues in the environment is the elimination of large number of heavy metals from industries waste into the natural water. At high level, exposure to metals such as cobalt might lead to serious health problems and cause several diseases for human and animals including heart, lung and skin (Ali et al., 2021, Hussain et al., 2021, Kazi, et al., 2012). Consequently, it is essential to detect and determine cobalt element in different samples such as food and water. It's worth mentioning that, many analytical techniques comprising atomic absorption spectroscopy (AAS) and ICP-MS have been applied for the determination cobalt along other heavy metal in various samples (Alorabi, 2022, El-Zomrawy,

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Scheme 1. Synthesis of naphthalene and fluorene based azo dyes R1 and R2: (a) CH_3COCl , $AlCl_3$, DCM, 0 °C/ 6 h then rt/ overnight; (b) Cu_2Br_2 , $CHCl_3/CH_3/CH_3CO_2C_2H_5/$ rt/ reflux/ 9 h; (c) 1.1 eq. $H_2NCSNH_2/$ EtOH, reflux/ 4 h; (d) $NaNO_2/HCl/\beta$ -naphthol/NaOH.

2018, Khan and Kazmi, 1979). Nevertheless, these analytical instruments are expensive and time consuming. Accordingly, emerging a simple, selective, sensitive, inexpensive, and non-extractive spectrophotometric method is indispensable and needed to determine the heavy metal concentration, via an economical spectrophotometric assay (Alorabi, 2022, Dhaka et al., 2015, Echioda et al., 2021, Hatam et al., 2020, Khedr et al., 2010, Zhang et al., 2018). In this study, two new azo dye reagents were used at optimum parameters in order to determine cobalt ion through chelation with these reagents, namely, 1-[5-(9H-Fluoren-2-yl)-thiazol-2-ylazo]-naphthalen-2-ol, (R1) and 1-(5-Pyren-1-ylthiazol –2-ylazo)-naphthalen-2-ol, (R2). The effect of several experimental variables on the sensitivity and stability of the method was examined. The approach herein was applied for Co(II) determination in some spiked local water samples.

2. Experimental

2.1. Instrumentation

A Shimadzu UV-1800 spectrophotometer was used to acquire all UV–visible spectra. Melting points (uncorrected) were measured on SMP3 melting point apparatus. A Shimadzu FT-IR3600 spectrophotometer was used to collect IR spectra (KBr). All ¹H, ¹³C, Dept-135 NMR spectra were obtained on Bruker Avance 600 (at 600, 100, 135 MHz for ¹H, ¹³C and dept, respectively) in fully deuterated chloroform (CDCl₃) and DMSO-*d*₆. The pH for the used solutions was adjusted using pH-meter (METTLER TOLEDO MP220).

2.2. Reagent and materials

In this study, all solvents and chemicals were used without any further purification. Several buffer solutions were prepared according to the pervious method of Gomori (Gomorie, 1955). These prepared buffers included acetate, phosphate, borate and universal buffers. A stock solution of 1.0×10^{-3} M cobalt (II) nitrate hexahydrate, $Co(NO_3)_2 \cdot 6H_2O$, was prepared by dissolving an appropriate amount of the cobalt nitrate in a 100 mL measuring flask using bidistilled water. A working stock solution of 1.0×10^{-3} M were prepared by dissolving an appropriate amount of the investigated reagents 1-[5-(9H-fluoren-2-yl)-thiazol-2-ylazo]-naphthalen-2-ol, (R1) and 1-(5-pyren-1-yl-thiazol-2-ylazo)-naphthalen-2-ol, (R2) in absolute ethanol. From these stock solutions, fresh diluted solutions were prepared regularly. 0.5 % (v/v) solution of Triton X-100 and 0.5 % (w/v) solution of sodium dodecyl sulphate (SDS) were prepared. These solutions were prepared by dissolving an

appropriate amount of each surfactant in 100 mL bidistilled water. Hydrochloric acid, HCl (37 %, 1.2 g/mL) and NaOH (97.0 %, pellets) were obtained from Sigma-Aldrich.

2.3. Synthesis of (E)-1-((5-(9H-fluoren-2-yl)thiazol-2-yl)diazenyl) naphthalen-2-ol (5a,R1) and/or (E)-1-((5-(pyren-4-yl)thiazol-2-yl) diazenyl)naphthalen-2-ol (5b,R2)

The synthesis of (E)-1-((5-(9H-fluoren-2-yl)thiazol-2-yl)diazenyl) naphthalen-2-ol (R1) and (E)-1-((5-(pyren-4-yl)thiazol-2-yl)diazenyl) naphthalen-2-ol (R2) was undertaken (scheme 1). As shown, a Friedel-Crafts acylation of fluorene 1a and/or pyrene 1b gave 1-(9H-fluoren-2-yl) ethanone (2a) and 1-(pyren-1-yl) ethanone (2b) in 86-92 % yield, respectively. Next, bromination of acetylated compounds 2a,b performed utilizing cuprous bromide as brominating agent in refluxing CHCl₃/CH₃CO₂C₂H₅ for 9 h, to afford 2-bromo-1-(9H-fluoren-2-yl)ethanone (3a) and 2-bromo-1-(pyren-1-yl)ethanone (3b) in 81-93 % yields. On the other hand, the aminothiazole derivatives 4ab were obtained in 73-86 % yields as yellow crystals by refluxing compounds 3a, b with thiourea (1.1 eq.) in EtOH for 4 h. Products 4a, b were obtained as vellow crystals after recrystallization in ethanol. Finally the target azo dves R1 and R2 were obtained via diazotization of the corresponding 2aminothizole derivatives with freshly generated nitrous acid from NaNO₂/ HCl at 0–5 °C. Coupling of the diazonium salt with β -naphthol in basic media (aq. NaOH) at 0-5 °C afforded the anticipated coupled products (E)-1-((5-(9H-fluoren-2-yl)thiazol-2-yl)diazenyl)naphthalen-2-ol (R1) and (E)-1-((5-(pyren-4-yl)thiazol-2-yl)diazenyl) naphthalen-2ol (R2) as red-brown solid precipitate in 76-87 % yield, respectively. Both analytical and spectroscopic tools were used to characterize the synthesized compounds 2-4, R1 and R2 (see experimental section and supporting information).

2.3.1. Synthesis of 1-(9H-fluoren-2-yl)ethenone (2a)and/or 1-(pyren-1-yl) ethanone (2a,b)(Weng et al., 2012)

In an ice-cold bath, solution of fluorene (1a) and/or pyrene (1b) (100 mmol) in 250 mL CH_2Cl_2 was introduced drop by drop over a period of 2.5 h into an iced solution containing a mixture of 17.8 g of aluminum trichloride (132 mmol) and 9.6 mL of acetyl chloride (equimolar) dissolved in 30 mL of CH_2Cl_2 . The resulting mixture was gently stirred at 0 °C for 6 h and then allowed to stand at room temperature overnight. Subsequently, the mixture was slowly poured into 500 L of deionized water to which 100 mL of concentrated hydrochloric acid was added, and the resulting solution was stirred for a period of 3 h. The complex formed during this process was then decomposed, yielding a

clear yellow solution. The organic layer was separated, treated with anhydrous $MgSO_4$, then filtered and evaporated in vacuo. The resulting product was purified on silica gel (elution: DCM) to give the titled compounds **2a**, **b** in 86–92 yield, respectively.

1-(9H-fluoren-2-yl)ethenone 2a: Light-yellow crystals; mp 102–103 °C. IR (KBr): $\nu_{max} = 3090, 2899, 1679$ (carbonyl), 1632 (imine) cm $^{-1.1}$ H NMR (500 MHz, CDCl₃): δ 9.19 (1H, s, fluorene-H), 8.02 (1H, s, fluorene-H), 7.86 (2H, s, fluorene-H), 7.61 (1H, s, fluorene-H), 7.43–7.41 (2H, t, J = 1.78 Hz, fluorene-H), 3.97 (s, 2H, CH₂, 9H-fluorene), 2.68 (3H, s, CH₃); 13 C NMR (125 MHz, CDCl₃): δ 198.05 (carbonyl), 146.45 (C), 144.54 (C), 143.33C), 140.50 (C), 135.63 (CH), 128.05 (CH), 127.77 (CH), 127.09 (C), 125.97 (C), 124.97 (CH), 120.91 (CH), 119.86, 36.90 (CH₂), 26.81 (CH₃) ppm.

1-(pyren-1-yl)ethenone 2b: Yellow crystals; mp 86–88 °C. IR (KBr): ν max = 3082, 2927, 1686 (carbonyl), 1632 (C = C) cm^{-1.1}H NMR (600 MHz, DMSO): δ 8.90 (¹H, d, pyrene-H), 8.51 (1H, d, J = 6.45 Hz pyrene-H), 8.31–8.33 (2H, t, J = 2.78 Hz pyrene-H), 8.23–8.27 (3H, q, pyrene-H), 8.16 (1H, d, J = 6.50.78 Hz pyrene-H), 8.07–8.10 (t, 1H, J = 2.45 Hz, pyrene-H), 2.85 (3H, s, CH₃); ¹³C NMR (100 MHz, DMSO): δ 202.43 (carbonyl), 133.76 (C), 132.15 (C), 131.03C), 130.30 (C), 129.88 (CH), 129.82 (CH), 128.82 (CH), 127.55 (CH), 127.13 (CH), 126.94 (CH), 126.49 (CH), 124.78 (CH), 123.87 (CH), 30.94 (CH₃) ppm.

2.3.2. Synthesis of 2-bromo-1-(9H-fluoren-2-yl)ethanone (3a) and/or 2-bromo-1-(pyren-1-yl)ethenone (3b)(El Guesmi et al., 2020)

To a refluxing suspension of copper(I) bromide (17.22 g, 120 mmol) in 250 mL of ethyl acetate was added a solution containing 1-(9H-fluoren-2-yl)ethanone **2a** and/or 1-(pyren-1-yl)ethenone **2b** (100 mmol) in CHCl₃ (0.1 L) was gently introduced over a span of 50 min. The resultant solution was maintained at reflux for a duration of 9 h. and subsequently, while still hot, it was filtered through Celite, approximately 1 in. in thickness. The filter cake was thoroughly rinsed multiple times with EtOAc, and the combined filtrate was removed under vacuo to afford products **3a** and **3b** as buff color solid in 81–93 % yield. The obtained product we pure enough and used for the next step without further purification.

2-bromo-1-(9H-fluoren-2-yl)ethanone (**3a**): Yellow needles, mp 128–130 °C. IR (KBr): ν max = 3122, 2925, 1678 (carbonyl), 1632 (imine) cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 8.11 (¹H, s, fluorene-H), 7.95 (1H, s, fluorene-H), 7.89 (2H, s, fluorene-H), 7.63 (1H, s, fluorene-H), 7.46 (2H, t, *J* = 6.78 Hz fluorene-H), 4.14 (s, 2H, CH₂), 3.98 (2H, s, CH₂, 9H-fluorene); ¹³C NMR (125 MHz, CDCl₃): δ 186.77 (carbonyl), 148.13 (C), 144.71 (C), 143.80 (C), 139.95 (C), 128.76 (CH), 127.95 (CH), 127.32 (CH), 125.97 (CH), 125.40 (CH), 125.14 (CH), 121.26 (CH), 120.14 (CH), 36.89 (CH₂), 29.49 (CH₂, 9H-fluorene) ppm. Anal. Calcd. for C₁₅H₁₁BrO (287.15): C, 62.74; H, 3.86; Br, 27.83. Found: C, 62.72; H, 3.85; Br, 27.97 %.

2-bromo-1-(pyren-1-yl)ethenone (**3b**): Yellow crystals, mp 134–135 °C. IR (KBr): ν max = 3038, 2887, 1670 (carbonyl), 1628 (imine) cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ 9.18 (¹H, d, *J* = 5.90 Hz pyrene-H), 8.56 (¹H, d, *J* = 5.92 Hz pyrene-H), 8.47–8.45 (3H, m, pyrene-H), 8.38–8.32 (2H, m, pyrene-H), 8.30–8.25 (2H, m, pyrene-H), 4.98 (2H, s, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ 189.82 (C,O), 129.84, 126.19, 125.84, 125.67, 125.55, 125.44, 123.54, 122.25, 122.06, 121.98, 121.84, 121.75, 120.23, 119.84, 119.25, 119.18, 29.57 (CH₂) ppm. Anal. Calcd. for C₁₈H₁₁BrO (323.18): C, 66.89; H, 3.43; Br, 24.72. Found: C, 66.85; H, 3.41; Br, 24.64 %.

2.3.3. Synthesis of 4-(9H-fluoren-2-yl)thiazol-2-amine (4a) and/or 5-(pyren-4-yl)thiazol-2-amine (4b)

To a clear solution of 2-bromo-1-(9H-fluoren-2-yl)ethenone and/or 2-bromo-1-(pyren-1-yl)ethenone (**3b**) (30 mmol) in EtOH (200 mL), obtained by heating to reflux, was added an ethanolic solution (50 mL) of thiourea (2.66 g), introduced dropwise over a period of 30 min. The reaction was maintained at reflux for 4 h and subsequently allowed to cool to room temperature. The precipitate that formed during cooling

was rinsed with a sodium bicarbonate solution until no further effervescence was observed. The resulting solid was then filtered and dried in vacuum oven (2d), affording compounds **4a** and **4b** in 73 %-86 % yields. The obtained product we pure enough and used for the next step without further purification.

4-(9H-fluoren-2-yl)thiazol-2-amine (4a): Yellow crystals; mp = 169–172 °C. IR (KBr): νmax = 3265, 3175 (NH₂), 3056, 2898, 1620 (imine) cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 8.01 (1H, s, thiazole), 7.86 (2H, s, fluorene-H), 7.59 (1H, s, fluorene-H), 7.38 (1H, s, fluorene-H), 7.31 (1H, s, fluorene-H), 7.06 (2H, t, J = 2.46 Hz fluorene-H), 3.95 (2H, s, CH₂, 9H-fluorene), NH₂ protons is not showing up due to hydrogen bond formation and π-stacking as well; ¹³C NMR (125 MHz, CDCl₃): δ 168.56 (C), 150.63 (C), 143.69 (C), 143.73 (C), 141.40 (C), 134.13 (C), 122.28 (CH), 127.14 (CH), 125.60 (CH), 124.90 (CH), 122.73 (CH), 120.44 (CH), 120.41 (CH), 101.71(C), 39.41 (CH₂, 9H-fluorene) ppm. Anal. Calcd. for C₁₆H₁₂N₂S (264.34): C, 72.70; H, 4.58; N, 10.60; S, 12.13 Found: C, 72.69; H, 4.55; N, 10.57.97; S, 12.10 %.

5-(pyren-4-yl)thiazol-2-amine (**4b**): Pale yellow powder; mp = 188–189 °C. IR (KBr): ν max = 3264, 3174 (NH₂), 3044, 1627 (C,N) cm⁻¹; ¹H NMR (600 MHz, DMSO-*d*₆): δ 8.87 (1H, d, *J* = 2.46 Hz, pyrene-H), 8.27–8.24 (4H, m, pyrene-H), 8.19–8.14 (3H, m, pyrene-H), 8.09–8.05 (1H, m, pyrene-H), 7.29 (2H, s, NH₂), 6.96 (1H, s, thiazole-H); ¹³C NMR (100 MHz, CDCl₃): δ 168.74 (C,N), 150.71 (C), 131.43 (C), 130.90 (C), 130.71 (C), 128.21 (C), 127.83 (CH), 127.81 (CH), 127.74, (CH), 126.76 (CH), 126.19 (CH), 125.71 (CH), 125.41 (C),125.29 (C), 124.50 (C), 106.30 (CH-thiazole) ppm. Anal. Calcd. for C₁₉H₁₂N₂S (300.38): C, 75.97; H, 4.03; N, 9.33; S, 10.67. Found: C, 75.91; H, 3.97; N, 9.29; S, 10.73 %.

2.3.4. Synthesis of (E)-1-((5-(9H-fluoren-2-yl)thiazol-2-yl)diazenyl) naphthalen-2-ol (R1) and/or (E)-1-((5-(pyren-4-yl)thiazol-2-yl)diazenyl) naphthalen-2-ol (R2)

In 250 mL conical flask, 2.0 g of aminothiazole derivatives 4a, b was dissolved in 26.6 mL of 50 % (v:v) HCl. The solution was cooled-down in ice-bath with vigorous stirring till the reaction solution reaches a temperature of 0-3 °C. In another conical flask, a solution of sodium nitrite (3.4 g) in dissolved in 17 mL bidistilled water was chilled in an ice-bath at 0 °C. Then, sodium nitrite solution was added dropwise to the aminothiazoles 4a, b solutions under vigorous stirring. After the complete addition of sodium nitrite solution, the diazonium salts were formed and kept in the ice-bath for 15 min. In another 250 mL conical flask, 6.24 g β-naphthol was dissolved in 50 mL of 20 % NaOH solution, and the naphthol solution was cooled in ice-bath for 15 min. The cold diazonium salt solution was then slowly added to the β -naphthol solution under continuous stirring and the reaction temperature must kept below 5 °C after complete addition of diazonium salt by adding crushed ice from time to time for 30 min to assure the complete coupling and formation of the desired azo dyes, R1 and R2. A red-brown color acquires and solid crude fluorene and pyrene azo- β -naphthols R1 and R2 were precipitated. The reaction mixtures were left to stand for 2 h while being stirred to ensure the completion of the reaction. Subsequently, they were transferred to a refrigerator and left overnight. The red-brown solid products were decanted into a Büchner funnel under reduced pressure and washed 5x100 mL times with ice-cold water until the filtrate became clear. The solid products were dried under vacuum desiccator in absence of light for 2 days and the dried azo dye products were recrystallized from ethanol to afford the products R1 and R2 in 76-87 % yields.

(*E*)-1-((5-(9H-fluoren-2-yl)thiazol-2-yl)diazenyl)naphthalen-2-ol (**R1**): Red-brown; mp = 232–234 °C. IR (KBr): ν max = 3321 (OH), 3059, 2980, 2196 (N = N), 1627 (C,N) cm⁻¹, ¹H NMR (600 MHz, DMSO-*d*₆): δ 8.01 (s, 1H, thiazole), 7.98 (d, 1H, *J* = 6.76 Hz Naphthol), 7.94 (d, 1H, *J* = 6.76 Hz, Naphthol), 7.98 (d, 1H, *J* = 6.76 Hz, Naphthol), 7.94 (d, 1H, *J* = 6.80 Hz, Naphthol), 7.83 (d, 1H, *J* = 6.80 Hz, Naphthol), 7.75 (2H, d, *J* = 6.80 Hz, fluorene-H), 7.61 (2H, d, *J* = 6.76 Hz fluorene-H), 7.33 (1H, s, fluorene-H), 7.25 (1H, d, *J* = 6.76 Hz fluorene-H), 6.42 (s, broad, 1H, OH), 3.99 (2H, s, CH₂, 9H-fluorene); ¹³C NMR (100 MHz, DMSO-*d*₆): δ

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170.27 (C), 155.77 (C), 144.12 (C), 143.91 (C), 140.88 (C), 130.91 (C), 130.56 (C), 129.73 (C), 127.71 (CH), 127.34 (CH), 125.70 (CH), 125.06 (CH), 123.07 (CH), 122.28 (CH), 120.87 (CH), 119.08 (CH), 109.10 (CH), 102.28 (C), 36.90 (CH₂, 9H-fluorene) ppm. Anal. Calcd. for $C_{26}H_{17}N_3OS$ (419.50): C, 74.44; H, 4.08; N, 10.02; S, 7.64, Found: C, 74.45; H, 4.03; N, 10.11; S, 7.60 %.

(*E*)-1-((5-(pyren-4-yl)thiazol-2-yl)diazenyl)naphthalen-2-ol (**R2**): Red-brown powder; mp = 269–271 °C. IR (KBr): ν max = 3329 (OH), 3068, 1637 (C,N) cm⁻¹; ¹H NMR (600 MHz, DMSO-*d*₆): δ 8.66 (1H, d, *J* = 4.80 Hz, pyrene-H), 8.30–8.33 (4H, m, pyrene-H), 8.21–8.23 (4H, m, pyrene-H), 8.09–8.11 (2H, t, *J* = 1.76 Hz Napthol), 7.73–7.76 (1H, m, Naphthol), 7.60 (1H, s, thiazole-H), 7.52–7.54 (2H, m, Naphthol);7.06 (1H, s, Naphthol), 6.45 (s, broad, 1H, OH); ¹³C NMR (100 MHz, DMSO-*d*₆): d 169.34 (C,N), 158.78 (C), 131.78 (C), 131.19 (C), 130.90 (C), 130.82 (C), 130.54 (C), 129.74 (C), 128.52 (C), 128.24 (CH), 128.16 (CH), 128.12 (CH), 127.99 (CH), 127.88 (CH), 127.78, (CH), 126.95 (CH), 126.56 (CH), 126.44 (CH), 126.00 (CH), 125.70 (CH), 125.57 (C), 125.57 (C), 125.27 (C), 124.60 (C), 124.32 (C), 119.09(C), 109.11 (CHthiazole) ppm. Anal. Calcd. for C₂₉H₁₇N₃OS (455.53): C, 76.46; H, 3.76; N, 9.22; S, 7.04. Found: C, 76.53; H, 3.70; N, 9.19; S, 7.06 %.

2.4. General procedure

2.4.1. Solvent effect of the free reagents

The absorption spectra of the reagents R1 and R2 were investigated by measuring the reagents in different kind of solvents in order to examine a various parameters such as dielectric constant, refractive index, and H-bonding capacity (Avc1 et al., 2016, Sayqal et al., 2020). The effect of different organic solvents (*e.g.*, ethanol, methanol, dimethylformamide, acetonitrile, acetone, and hexane) were studied by measuring the absorption of 1.0×10^{-5} M solution of each reagent in these solvents against a pure solvent as a blank within a UV/Vis spectrum.

2.4.2. Spectrophotometric studies of complexes between Co(II) and the studied reagents

To establish the optimum conditions between Co(II) and reagents R1 and R2, numerous parameters such as concentration of reagents, wavelength, pH, buffers, time, sequence of addition, and temperature were investigated. The solution of the complexes formed between the two reagents and Co(II) were prepared by mixing 4.0 mL of 1.0×10^{-3} M R1 and 2.5 mL of 1.0×10^{-3} M R2 with 0.5 mL of 1.0×10^{-3} M cobalt ion in 10 mL measuring flask comprehending optimum buffer solution of the optimum pH. The absorbance of these mixtures were measured against a blank solution prepared by the same manner except of the metal ion, at λ_{max} 472 and 470 nm for Co(II)-R1 and Co(II)-R2, respectively. In addition, the influences of time on the obtained complexes between the reagents and the metal ion were examined at different time intervals. Also, the effect of temperature was investigated at various temperature ranges 23–55 °C using thermoelectrically temperature controlled, Shimadzu UV-1800 spectrophotometer.

2.5. Measurement of the nature of Co(II) complexes

For the determination of the stoichiometric ratio, Job's procedure of continuous variation was used to track the generation of the complexes between R1 and R2 reagents with cobalt ion (Job, 1928). In this method, at optimum conditions, the cobalt ion was mixed with a series of 10 mL portions of each reagent solution separately. These mixture solutions represent different complementary proportions, and they were subsequently processed as per the prescribed protocol. To determine the stoichiometric proportions of the obtained complexes, the line intersections were calculated from the plot between the mole fraction of Co(II) and the measured absorbance signal.



0.0 250 300 350 400 450 Wavelength, nm

Fig. 1. The electronic absorption spectra for 1.0×10^{-5} M solution for reagent R1 and R2 in different organic solvent against a pure organic solvent as a blank.

2.6. Analytical application

To investigate the validation of the suggested approach, cobalt ion was measured in some water samples. All water samples were spiked with cobalt ion prior analysis. Tap water samples were collected from the laboratory at Umm Al-Qura University, whereas the wastewater samples were provided from a local wastewater treatments plant in Makkah region. An aliquot of standard solution of cobalt ion at the obtainable linearity range was transferred to each real tap water or wastewater sample. Samples were then investigated by the presented two approaches.

3. Results and discussion

A spectrophotometric assay is one of the most common analytical assay dependents on colorimetric properties of some compounds (Akram et al., 2020, Coulibaly, 2021, El-Zomrawy, 2018, Hatam, et al., 2020), Many compounds are characterized by their property to completely coordinate metal ion forming chelates. In this study, we report some results of this colorimetric assay using coupling with some prepared fluorophores based azo dyes that were effectively used to determine the concentration of Co(II) ion.

3.1. Solvatochromic properties of R1 and R2

Fig. 1 showed the impact of investigated solvents on the UV/Vis spectra for 1.0×10^{-5} M of the studied reagents, the resulted spectra of each reagent was collected by measuring the absorbance of reagents in organic solvents against a pure solvent as a blank solution. The obtained results confirm that, the absorption spectra of the exploited reagents are influenced by all the used solvents. The recorded bathochromic, red shifts, of the organic solutions absorption signals are understood as indication of changing of the series of structurally-related organic

Table 1

UV/Visible spectral parameters for R1 and R2 in some organic solvent.

Solvent	Parameter*	R1			R2						
		Peak No.			Peak No.						
		1	2	3	1	2	3	4	5		
Ethanol	λ_{max} , nm	264	319	371	232	242	265	276	346		
	ϵ , L mol ⁻¹ cm ⁻¹	2.83	1.65	0.72	9.64	10.44	5.91	6.16	4.31		
Methanol	λ_{max} , nm	263	313	365	232	241	265	276	343		
	ϵ , L mol ⁻¹ cm ⁻¹	2.20	1.23	0.47	8.52	9.08	5.21	5.47	4.06		
DMF ^{**}	λ_{max} , nm	_	307	369	_	_	_	277	352		
	ϵ , L mol ⁻¹ cm ⁻¹	_	1.45	0.67	_	_	_	2.79	1.81		
Acetone	λ_{max} , nm	_	_	368	_	_	_	_	354		
	ϵ , L mol ⁻¹ cm ⁻¹	_	_	0.73	_	_	_	_	3.25		
Acetonitrile	λ_{max} , nm	270	317	370	232	241	_	275	352		
	ϵ , L mol ⁻¹ cm ⁻¹	2.71	1.62	0.83	5.58	5.56	_	3.85	2.38		
Hexane	λ_{max} , nm	273	_	370	220	_	_	273	370		
	ϵ , L mol ⁻¹ cm ⁻¹	0.39	—	0.17	2.23	—	—	1.44	0.64		

* ε : The molar absorptivity $\times 10^4$.

**DMF: Dimethylformamide.

DMI¹. Dimentynormannud



Fig. 2. Absorption spectra for the Co(II) complex between Co(II) and reagents (R1 and R2) where A) is the absorption spectrum for 1.0 mL of 1.0×10^{-3} M reagent and universal buffer against buffer, B) the absorption spectrum for 0.5 mL 1.0×10^{-3} M Co(II), 1.0 mL of 1.0×10^{-3} M reagent and buffer against buffer, C) the absorption spectrum for 0.5 mL of 1.0×10^{-3} M Co(II), 2.5 mL of 1.0×10^{-3} M reagent and buffer against buffer.

molecules or the kind of organic solvents polarities (Masoud et al., 2005, Sayqal, et al., 2020, Yazdanbakhsh and Mohammadi, 2009). The studied solvents were selected based on the diversity of solvent parameters (Sayqal, et al., 2020). Table 1, showed the molar absorptivity at the different λ_{max} for each reagent in the used solvents. Predominantly,

three absorption peaks were observed for R1 within the range 200-450 nm using most used solvents while for reagent R2, five peaks with different intensities were presented. After comparing the peaks at longer wavelength for both R1 and R2, which located around 370 nm for R1 and 350 nm for R2, a high molar absorptivity for R2 was observed using all solvents where for ethanol and methanol, as examples, equals 4.31×10^4 and 4.06×10^4 L mol⁻¹ cm⁻¹ for R2 and 0.72×10^4 and 0.47×10^4 $L \text{ mol}^{-1} \text{ cm}^{-1}$ for R1, respectively. As seen from Fig. 1, the two reagents under investigation have dissimilar absorption region. Therefore, it is clear that each absorption peak's position and intensity was changed due to the diversity of solvent's polarity. In general, the position of the absorption peaks for all synthesized organic reagents shifts to higher wavelengths (bathochromic shift,) as solvent polarity increases (Yazdanbakhsh and Mohammadi 2009). This performance is elucidated by the fact that molecules in the ground and excited states exhibit different polarities. For the reagents (R1 and R1) with positive inductive groups on the thiazole moiety, a solvatochromism take place in the $(n \rightarrow \pi^*)$ absorption due to the increase of the push-pull character of the groups (Masoud, et al., 2005). These findings emphatically affirm the notion that the examined substances are likely to exhibit strong chromophoric signals.

3.2. Spectrophotometric studies for Co(II) complexes with the studied reagents

In order to investigate the relation between cobalt ion and the studied reagents, UV/Vis spectra were collected. As seen in Fig. 2 (a.b), the absorption spectra of free reagents R1 and R2 in a universal buffer exhibits absorption peaks in the ultraviolet region at λ_{max} 358 and 360 nm, respectively. Upon binding of reagents R1 and R2 with Co(II) ions, it was found that the spectra have some bathochromic shift of the absorption peaks with a change in the absorbance. This clear observation is due to formation of the complex which resulted from the addition of the cobalt ion to the investigated reagents (El-Zomrawy, 2018, Mostafa et al., 2021). In case of curve (C) in both complexes, where the blank solution was (the used reagent and the buffer), a clear peaks for the formed Co(II) were obtained in the visible region at λ_{max} 472 and 470 nm, respectively. This is bathochromic shift due to the complexation between Co (II) and the considered reagents indicating the formation of stable Co (II)-R1 and Co(II)-R2 complexes.

3.3. Optimum conditions for spectrophotometric determination of Co(II)

3.3.1. Effect of pH on Co(II) complex

For recognizing the most suitable buffer and the optimum pH used to achieve a maximum cobalt complex stability appeared in the highest



Fig. 3. The effect of pH of universal buffer on the absorption intenistry for Co (II) complex between 1.0 mL of 1.0×10^{-3} M Co(II) and 1.0 mL of 1.0×10^{-3} M reagent solution.



Fig. 4. The volume effect of 1.0×10^{-3} M solution of R1 and R2 on the absorption spectra for Co(II) complexes using 0.5 mL of 1.0×10^{-3} M Co(II).

absorbance and most obvious peak, different kinds of buffer solutions were studied for complex formation between cobalt and the two previously prepared reagents, R1 and R2. In addition, Fig. 3 was designated to show the effect of pH values of universal buffer solutions on the Co(II) complexes. Particularly, the increase of absorbance appeared with increasing pH and gave the highest absorbance at pH 8.97 for Co(II)-R1 and pH 10.98 for Co(II)-R1. As seen, the use of alkaline medium produced the best results for the Co(II) complexes under investigation. An increase in the absorption intensity at optimum pH values was reached to the optimal value after adding 3.0 mL of pH 8.97 for Co(II)-R1 and 4.0 mL of pH 10.97 for Co(II)-R2 using a universal buffer solution.

3.3.2. Effect of reagent volume

The best reagent volume for the cobalt complexes with R1 and R2 was investigated and determined in this study. The reagent volumes were varied in a range of 1.0-5 mL of 1.0×10^{-3} M reagent concentration as shown in Fig. 4. For Co(II)-R1 complex, the use of 4.0 mL from R1 reagent gave a high stability and orange color development while at lower volumes, the absorbance decreased. Whereas, a 2.5 mL of 1.0×10^{-3} M of R2 was the optimum in case of Co(II)-R2 complex.

3.3.3. Effect of surfactants

The effect of different types and different volumes (0.5, 1.0, 1.5 mL) 0.5 % (w/v), for SDS and 0.5 % (v/v) for Triton X-100, and Tween-20 on the absorbance of Co(II)-R1 and Co(II)–R2 complexes was studied, and it



Fig. 5. Job s process of continuous variation for Co(II) complexes with R1 and R2 at the optimum conditions.

showed no predictable effect in this study and did not affect the method sensitivity.

3.3.4. Influence of sequence of addition

The study also examined the impact of varying the sequence of addition during the complex formation between Co(II) and the two reagents, as this could potentially yield insightful findings. Interestingly, different sequence orders of mixing the reagents, cobalt ion, and buffering solution revealed that the most effective order which produced the highest absorption for cobalt complexes with R1 and R2 was (Co(II)-buffer-R1) and (Co(II)-R2-buffer), respectively. Other achievable orders of addition present not perfect peaks with a low absorbance response. Notably, experimenting with different sequence orders for combining the reagents, cobalt ion, and buffering solution yielded interesting results. It was found that the most effective sequences, which produced the highest absorption for cobalt complexes with R1 and R2, were (Co(II)-buffer-R1) and (Co(II)-R2-buffer), respectively.

3.3.5. Effect of temperature and time

To investigate the influence of time on the peak intensity of the cobalt complex at its maximum wavelength, (optimum conditions), the absorbance value was measured at different time intervals up to 30 min. The obtained results for R1-Co(II) complex found that six minutes is an appropriate time to reach the optimum absorbance properties. While in the case of R2 complexes, four minutes were required to reach a stable value of absorbance and a perfect peak. Furthermore, to elucidate the influence of temperature on cobalt complexes absorbance, different temperatures between 23 °C and 55 °C were examined. The results showed an obvious steady absorbance for all cobalt complexes at different temperature. Therefore, 23 °C was selected to perform all the measurements.

3.4. Determination of stoichiometric ratio

The stoichiometric ratios of the ion–associate complexes generated between the investigated cobalt ion and the azo dyes species were found by applying the continuous variation method (Gouda et al., 2016, Job, 1928). Fig. 5 represents the stoichiometric ratio for cobalt complexes with two reagents (R1 and R2) was (1:2) (Co(II):Reagent). The plot between absorbance and mole fraction of Co(II) shows that the intersections is at 0.3 and this finding support the stoichiometric ratio. Based on these results, the expected structure for cobalt complexes with the studied reagents are illustrated in Fig. 6.



Fig. 6. The (2:1) (R:Metal) structure for Co(II) complexes with R1 and R2 (X = fluorene moiety for R1 and pyrene moiety for R2).



Fig. 7. Calibration curve for determination of Co(II) using 4.0 mL of 1.0×10^{-3} M R1 after addition of 3.0 mL universal buffer of pH 8.97 and 2.5 mL of 1.0×10^{-3} M R2 after addition of 4.0 mL universal buffer of pH 10.98.

3.5. Validation of the developed methods

3.5.1. Statistical analytical parameters

By numerous methods of optimal complex formation parameters, the relationship between peaks and their absorbance's for the two synthesized azo dyes reagents and concentration of Co(II) is obtained. Fig. 7 (a, b) represents the calibration graph for spectrophotometric determination of cobalt ion with reagents R1 and R2, in that order.

Table 2 shows the statistics of the used two reagents with results showing that, the linearity range for micro determination of Co(II) utilizing the reagents R1 and R2 were 0.2–3.0 and 0.4–3.0 μ g mL⁻¹, respectively. The calibration curves of Co(II)-R1 and Co(II)-R2 complexes represent a good linearity with a correlation coefficient (r) 0.9929 and 0.994, in that order. The detection limit (LOD) and quantification

Table 2

The optimum conditions and statistics of data analysis for spectrophotometric determination of Co(II) using the R1 and R2.

Parameter	Co(II) – R1	Co(II) – R2
Color of complex	Orange	Orange
Type of buffers	Universal	Universal
Working pH	8.97	10.97
Volume of buffer, mL	3.0	4.0
Amount of reagent, 1×10^{-3} , mL	4	2.5
Sequence of addition	Co-B-R1	Co-R2-B
Time, min	6.0	4.0
λ_{max} (nm), A curve	358 nm	360 nm
λ_{max} (nm), B curve	424 nm	444 nm
λ_{max} (nm), C curve	472 nm	470 nm
Beer law range, (µg/mL)	0.2 - 3.0	0.4 - 3.0
Detection limit, (µg/mL)	0.034	0.025
Quantification limit, (µg/mL)	0.102	0.076
Standard deviation (SD)	0.018	0.045
Relative Standard deviation (RSD)	2.46 %	5.65 %
Variance	$3.37 imes10$ $^{-4}$	$2.0332 imes10^{-3}$
Error %	0.75	1.84
Slope	0.316	0.436
intercept	0.108	-0.099
Correlation coefficient	0.9929	0.994
Molar Absorptivity ($\times 10^4$ L mol $^{-1}$ cm $^{-1}$)	1.78	2.6
t-test 1	-1.33	0.434
Confidence limit ¹	$\pm \ 0.0192$	\pm 0.047

¹Confidence level 95 %, n = 6 and the theoretical value of *t* at 5 degree of freedom is 2.571.

(LOQ) were calculated according to IUPAC recommendations (Guideline, 2005). The LOD was found to be 0.034 and 0.025 and LOQ determined as 0.102 and 0.076 μ g mL⁻¹ in that order.

Table 3 showed a comparison between some previous studies for spectrophotometric quantification of Co(II) using reagents and our obtained results using R1 and R2. This comparison indicated that the obtained linear range, detection limit and molar absorptivity, are in a good agreement and reasonable values in the light previous methods (Akl Alharawi 2018, Chandravanshi Asgedom 1995, Devi Reddy 2012, Nassir, 2007, Rajni Usha 2012, Shaheed et al., 2016, Soomro Shar 2014, Sulaiman Hamoudi 2018). Despite the existence of prior spectrophotometric techniques and alternative approaches for cobalt ion estimation, the discovered method employing newly synthesized azo dyes reagents stands out for its ease of use, high sensitivity, and time-saving nature. Consequently, the proposed method for the determination of cobalt ions was conducted in a few actual samples, in order to verify its reliability and validity. Furthermore, the created approach was labor-saving as the performance of any extraction or the use of numerous chemicals is not required prior to analysis.

Table 3

Comparison of previous studies with the proposed methods.

Reagents used	R ²	Linear range, $\mu g \ m L^{-1}$	Detection limit, $\mu g m L^{-1}$	Molar absorptivity L mol^{-1} cm ⁻¹	Ref.
Azo dye reagent ^a Mordant Blue 9 HDPBA reagent ^b NNPh ^c MPAI ^d HNHB reagent ^e Alizarin Red S Azo dye reagent ^f R1 R2	- 0.999 - 0.9999 0.9999 0.9999 0.9997 0.9997 0.9964 0.9955	0.01-0.32 0.004-1 0.1-12 0.12-4.0 3.00-50.00 0.118-3.534 0.293-4.124 1-8 0.2-3.0 0.4-3.0	$\begin{array}{l} 3.09 \times 10^{-3} \\ 4.006 \times 10^{-3} \\ 0.04 \\ 0.12 \\ 2.083 \\ 0.04 \\ - \\ 0.2 \\ 0.034 \\ 0.025 \end{array}$	$\begin{array}{l} 1.5 \times 10^{4} \\ 3.97 \times 10^{4} \\ 7.0 \times 10^{3} \\ 2.05 \times 10^{4} \\ 0.2703 \times 10^{4} \\ 2.3 \times 10^{4} \\ - \\ 4857.1 \\ 1.78 \times 10^{4} \\ 2.6 \times 10^{4} \end{array}$	(Akl and Alharawi, 2018) (Sulaiman and Hamoudi, 2018) (Chandravanshi Asgedom 1995) (Soomro and Shar, 2014) (Shaheed et al., 2016) (Devi and Reddy, 2012) (Rajni and Usha, 2012) (Nassir, 2007) PM*

^a4-(2-Pyridyl azo) resorcinol.

^bN¹-Hydroxy-N¹, N²-diphenylbenzamidine.

^c1-Nitroso-2-naphthol.

^d2-(4-Methoxyphenyl) azo (4, 5-dipheny imidazole).

 $^{
m e}$ 2-Hydroxy-1-naphthaldehyde-p-hydroxybenzoichydrazone.

^f4-(6-Nitro-2-benzothiazolylazo) resorcinol.

^g The proposed methods.

Table 4 Analytic

Ana	lytical	appl	licatior	1 for o	determina	ation o	f (Co(II)) in	some sp	ikec	l water	sampl	les
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Sample	[CO(II)],	μg mL	Recovery 70			
	Added	Found + SD 1	—			
		R1	R2	R1	R2	
Tap water	-	n.f ²	n.f ²	-	_	
	0.5	0.502 ± 0.01652	0.514 \pm	100.4	102.8	
			0.015716			
	1	$0.976~\pm$	$1.002~\pm$	97.6	100.2	
		0.018148	0.017926			
	1.5	$1.483~\pm$	1.434 \pm	98.86	95.6	
		0.036005	0.024685			
	2	1.919 ± 0.03759	$1.985~\pm$	95.95	99.25	
			0.046519			
Wastewater	-	n.f ²	n.f ²	-	-	
	0.5	0.511 ± 0.02816	$0.487~\pm$	102.2	97.4	
			0.015011			
	1	$0.986~\pm$	$0.972~\pm$	98.6	97.2	
		0.018009	0.009292			
	1.5	1.435 \pm	1.432 \pm	95.66	95.4	
		0.026839	0.007638			
	2	$1.973~\pm$	1.924 \pm	98.65	96.2	
		0.028219	0.023502			

 1 Standard deviation for three replicates (n = 3).

² Not found.

3.5.2. Analytical applications

Based on the exceeding achieved methods and at the optimal conditions, Co(II) was spectrophotometric micro determined in some tap and wastewater samples. Table 4 represents data measured for spiked H_2O with a various quantity of Co(II), the average of recovery percent of the methods for all measurements were in the ambit of 99.1 % confirming that this assay can be applied to be used for determination of cobalt metal ions in different analytical samples with high degrees of efficacy and precision.

4. Conclusions

Utility of the two new synthesized azo dyes based fluorophores reagents, R1 and R2 were used successfully for spectrophotometric detection of cobalt ion. The structure of the prepared reagents was investigated and confirmed using ¹H NMR, ¹³C NMR and DEPT-135 NMR. The developed procedure based on a formation of stable complexes between Co(II) and R1 and R2. Based on this research, the stoichiometric ratio for the azo dye reagents and cobalt complexes was determined to be (1:2) (Co(II):reagent). The chelation between cobalt

and the used reagent was employed for the determination of cobalt in many spiked water samples, which can be easily determined with rapid, accurate, and cost-effective methods. The results obtained were highly accurate compared to previously published methods.

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CRediT authorship contribution statement

Ali Sayqal: Main idea, Conceptualization, Methodology, Data curation, Validation, Investigation, Visualization, Project administration, Supervision, Funding acquisition, Writing – review & editing the manuscript. Muthibah M. Alotaibi: Main idea, Conceptualization, Methodology, Data curation, Validation, Investigation, Visualization, Project administration, Supervision, Funding acquisition, Writing – review & editing the manuscript. Mohammed A. Kassem: Conceptualization, Methodology, Validation, Data curation and draft preparation. Saleh A. Ahmed: Conceptualization, Methodology, Data curation, Methodology, Data curation, Writing – review & editing the manuscript.

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Appendix A. Supplementary data

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