Development of a Simple Fe(II) Ion Colorimetric Sensor from the Immobilization of 1,10-Phenanthroline In Alginate/Pectin Film

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Abstract: *An optical analytical sensor was proposed based on the complexation reactions of 1,10-phenanthroline derivative in aqueous solutions. This study aims to synthesize a metal ion sensor for detecting Fe(ll) ion from the immobilization of 1,10-phenanthroline compound in alginate/pectin film. This was carried out by characterizing the films using the Fourier-transform infrared spectrometry (FT-IR) and scanning electron microscope (SEM). The determination of the optimal condition for Fe(II) ion detection and validation of the parameters was conducted by measuring the absorbance of the films using a UV-Vis spectrophotometer. After the addition of Fe(II) ion, the color of the alginate/pectin-phenanthroline film changed from transparent yellow to orange-red, showing its potential as a visual colorimetric sensor for iron(II) ion. It was found that the optimum condition for Fe(II) ion sensing was at 513 nm after 2 min of detection at pH 2. The alginate/pectin-phenanthroline film had good linearity, precision, selectivity, and accuracy with a detection limit as low as 0.446 mg L^{-1}, which was remarkable.*

Keywords: *alginate/pectin film; colorimetric sensor; Fe(II) ion detection; 1,10-phenanthroline*

■ INTRODUCTION

Iron (Fe) is one of the most essential heavy metals in the industrial field due to its low cost, sturdiness, and ease of mass production, which has made it an ideal choice for transportation, mining, and construction. However, the disposal of iron waste from various industrial activities, such as mining sports, hydrometallurgy, foundries, and smelters [1] into the aquatic environment, causes some adverse effects not only to the environment but also to human health. In the form of Fe(II) and Fe(III) ions, they are indispensable as the micronutrient for living organisms; however, they cause problems for ecosystems and human health at higher concentrations. According to the WHO regulation, the limit for Fe(II) and Fe(III) ions should be less than 0.3 mg L^{-1} in municipal drinking water [2]. When their amounts exceed this limit, they generate an unpleasant taste and odor in drinking water, causing tissue damage in humans and also blockage of pipes or transmission lines in the processing industry due to the formation of iron hydroxide precipitations [3].

Several analytical methods have been established for the determination of Fe ions concentration in environmental samples, such as atomic absorption spectrometry (AAS) [4], UV-Visible spectrophotometry [5], inductively coupled plasma-optical emission spectrometry (ICP-OES), and inductively coupled plasma-mass spectrometry (ICP-MS) [6]. However, these methods still have several limitations, such as complicated protocols, time and cost consumption, and requiring a specific technique. Therefore, a simple method for the determination of Fe ions is highly required. The colorimetric sensor becomes an extremely enticing method since it is easy to read using a low-cost portable instrument and even naked-eye observation [7].

Colorimetric methods are carried out using specific chemicals which are immobilized in a suitable matrix, where they selectively bind the analytes and produce characteristic color change [8]. The optical sensors for the analysis of Fe(II) ions have been previously developed using PVC-based membranes as a

matrix for immobilizing 2,6-bis(carboxamide methyl ester) as the chromogenic reagent [9]. However, these methods required complicated reagent synthesis processes. Similarly, a simple optical sensor was developed using the polypropylene-based paper strip with the immobilized 1,10-phenanthroline reagent [3]. However, this method uses a synthetic polymer-based matrix, which is less environmentally friendly.

In this study, a new film sensor for Fe(II) ion determination using a functionalized, environmentally friendly membrane was developed. This comprises of pectin, a polysaccharide composed of D-galacturonic acid monomers forming a long chain through 1,4-glycoside bonds, and commonly found on the plant cell walls [10]. And alginate, a hydrophilic polysaccharide composed of bonds (1,4) between β-D-mannuronate (M) and α-L-guluronate (G) copolymers, and commonly found in seaweed [11]. Both biomaterials are capable of forming strong gels in the presence of divalent cations, such as Ca^{2+} ion. The combination of these polymers provides unique properties that are strong, water-resistant, and are widely used in several fields as a carrier matrix [12]. Then, the 1,10-phenanthroline reagent is immobilized on the alginate/pectin film to obtain the functionalized optical membrane that provides a rapid, sensitive, and simple alternative method for determining Fe(II) in the aqueous sample.

■ EXPERIMENTAL SECTION

Materials

Sodium alginate was obtained from Sigma Aldrich. Mannuronic to the guluronic acid ratio (M/G) of alginate was 1.56. High methoxyl content pectin was procured from Bintang Utama Sentosa Inc. (Bekasi, Indonesia). Ethanol (99.9%) and 1,10-phenanthroline (99.9%) were purchased from Merck. Stock solution (100 mg L^{-1}) of Fe(II) ion 100 mL was prepared from the solid $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (Merck) 0.07 g, which was dissolved in distilled water by adding 0.50 g of hydroxylamine hydrochloride 99.9% (Merck) and 5 mL of H_2SO_4 (Merck) 2 M. Standard solution 1000 mg L^{-1} of Cu^{2+}, Zn^{2+}, Co^{2+}, Fe^{3+}, Pb^{2+}, Ni^{2+}, Ca^{2+}, and Mg^{2+} (Merck) were used for the interference study and prepared using distilled water

from CV. Progo Mulyo (Yogyakarta, Indonesia). All chemical used were analytical reagent grade without further purification process.

Instrumentation

The color absorbance of sensor films was determined using a UV-Vis Spectrophotometer (Shimadzu UV-1800). The prepared membrane was characterized by a Fourier Transform-Infrared Spectrophotometer (Shimadzu IR Prestige 21), while the morphology of surface membranes was analyzed using a Scanning Electron Microscope (JOEL type JSM-6701F).

Procedure

Synthesis of alginate/pectin film immobilized 1,10-phenanthroline

The alginate/pectin-phenanthroline film was made by mixing 0.05 g alginate and 0.20 g pectin in 10 mL of distilled water. The homogeneous solution was then poured into a petri dish (60 mm) and dried at 55 °C for 16 h. The alginate/pectin film was immersed for 24 h in a solution of 2% (w/v) $CaCl_2$ to allow the crosslinking reaction. The crosslinking alginate/pectin film was then immersed in 5 mL 1,10-phenanthroline for 24 h. After that, the obtained film was dried at room temperature and was used for further characterization. The thickness of the alginate/pectin-phenanthroline film was 0.029 ± 0.005 mm, with an average weight of 0.1258 g. For all the experiments, the film was cut into 1×1 cm^2 size and used.

Optimization of the measurement parameters

Colorimetric detection of Fe(II) ions using alginate/pectin-phenanthroline film was carried out by immersing the film in 2 mL of Fe(II) solution for 2 min. Various concentration (2–10 mg L^{-1}) of Fe(II) ion was adjusted at pH 1–6 using 0.1 M HCl and 0.1 M NaOH solutions. The maximum absorption wavelength of the alginate/pectin film was measured by scanning the absorbance of the film at 450–600 nm using a UV-Visible spectrophotometer. The λ_{max} was used to obtain the amount of phenanthroline to be added during the synthesis of the alginate/pectin film by varying the concentration of 1,10-phenanthroline (0.1–0.3% w/v). The interference study of alginate/pectin-phenanthroline film was investigated by performing the detection of

Fe(II) ion in the presence of other metal ions (Cu^{2+}, Zn^{2+}, Co^{2+}, Fe^{3+}, Pb^{2+}, Ni^{2+}, Ca^{2+}, and Mg^{2+}) under optimum condition.

Film alginate/pectin sensing ability

The different concentrations (0, 2.0, 4.0, 6.0, 8.0, and 10.0 mg L^{-1}) of Fe(II) solutions were tested using a film sensor in triplicate to obtain the calibration curve. The detection limit is calculated using the 3s/S criterion, where 's' is the standard deviation of the absorbance of 10 blank alginate/pectin film, and 'S' is the slope of the linear calibration curve [3]. The accuracy of the film sensor is determined based on the % recoveries of Fe(II) concentration added into the tap water sample. The tap water sample from the Laboratory of Analytical Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Yogyakarta, Indonesia, was used as a real water sample. The tap water was collected in a 1.5 L plastic bottle and was added with 50 mL of H_2SO_4 2 M and 5.0 g hydroxylamine hydrochloride. The sample was filtrated using Whatman filter paper 42. Fe(II) solution 100 mg L^{-1} (0.20, 0.50, and 1.00 mL) was spiked into the tap water sample in a 10 mL volumetric flask. All of the tap water samples were examined using the alginate/pectin film. The absorbance of the film was measured using a UV-Visible spectrophotometer under optimum condition. The % recoveries are calculated by comparing the concentration of Fe(II) obtained from the measurement with the concentration of Fe(II) added in the sample.

■ RESULTS AND DISCUSSION

FTIR Characterization of Alginate/Pectin-Phenanthroline Film

The FTIR spectra of alginate/pectin-phenanthroline film and the initial reagents were shown in Fig. 1. The spectrum of sodium alginate (see Fig. 1(a)) had a broad peak at 3320 cm^{-1} due to the stretching of O–H bond, while the sharp peaks between 1584–1413 cm^{-1} were attributed to the asymmetric and symmetrical vibration of COO^- respectively [13]. The FTIR spectrum of pectin (see Fig. 1(b)) had two bands that were associated with the stretching vibration of the carbonyl group (C=O) in the 1800–1500 cm^{-1} region. The band at 1731 cm^{-1} was

assigned to the methyl ester group ($-COOCH_3$), while the one observed at 1634 cm^{-1} originated from the asymmetric vibration of the carbonyl group in the carboxylate ion ($-COO^-$). The bands around 1065 cm^{-1} were associated with the stretching of the C–O–C bond [14].

The characteristic peaks of 1,10-phenanthroline commonly occur at 1620–1400 cm^{-1}, which were attributed to the stretching of C=C and C=N in the aromatic ring of phenanthroline [15] (see Fig. 1(c)). Meanwhile, a broad water band in the region of 3400 cm^{-1} was usually present on the FTIR spectrum of phenanthroline due to the highly hygroscopic nature of phenanthroline [16].

The crosslinking process with Ca^{2+} ions caused an obvious shift of $-COO^-$ asymmetric and symmetric stretching to higher wavenumbers in the alginate/pectin-phenanthroline spectrum (Fig. 1(d)). This indicated the formation of an ionic bond between $-COO^-$ from alginate and pectin and Ca^{2+} in order to form an "egg-box structure" [12]. The non-crosslinked alginate/pectin film containing the negatively charged carboxyl interacted with the positively charged proteins through electrostatic interaction [17]. Therefore, the protonated 1,10-phenanthroline, which was the positively
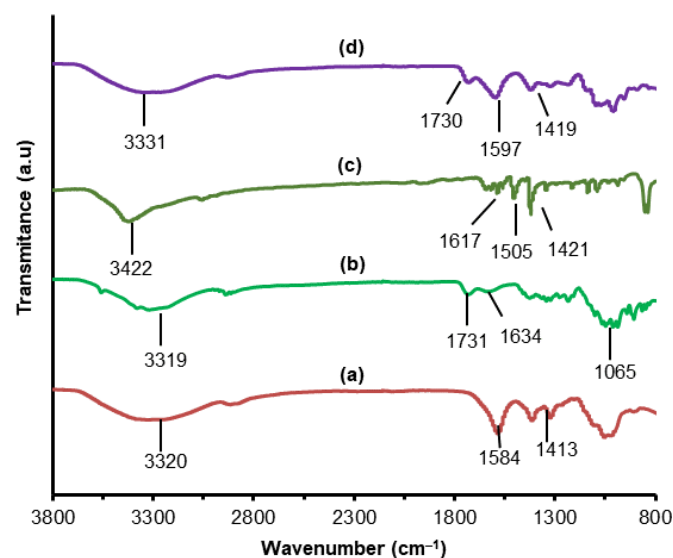

Fig 1. FTIR spectra of (a) sodium alginate, (b) pectin, (c) 1,10-phenanthroline, and (d) alginate/pectin-phenanthroline films

charged group, interacted with the alginate/pectin film through electrostatic interaction. Fig. 2 showed the proposed immobilization process of 1,10-phenanthroline in alginate/pectin film. There was no significant shifting on the methyl ester, indicating that this functional group did not involve in the interactions of alginate/pectin film with Ca^{2+} cation. The shifted peak from 3320 to 3331 cm^{-1} exhibited an overlap between the stretching of OH groups in the alginate/pectin polymers and the 1,10-phenanthroline spectrum.

The nature of alginate and pectin were known to be very hydrophilic since they consisted of many –OH and –COOH groups. The presence of divalent cations, such as Ca^{2+}, replaced the Na^+ ions in the sodium alginate and caused the polymer chains of alginate/pectin to cross-link [18]. This process increased the mechanical strength of alginate/pectin film, reducing its dissolution in water; however, it still has the ability to swelling. The film must be able to undergo the swelling process so that the Fe(II) ion presented in the solution may diffuse into the matrix in order to interact with the 1,10-phenanthroline reagent that is bound to the film matrix. In addition, films formed only from alginate are very soft, brittle, easily dissolve in water but visually more transparent than alginate/pectin films. In contrast, films made only from pectin are rigid but have yellow in color. The mixture of alginate and pectin then produces a stronger, more stable, and transparent film. The transparency of the alginate/pectin film must be preserved because the absorbance of the film will be measured using a UV-Vis spectrophotometer.

SEM Characterization of Alginate/Pectin-Phenanthroline Film

The morphology of alginate/pectin-phenanthroline films before (Fig. 3(a)) and after sensing (Fig. 3(b)) Fe(II) ion was analyzed using the SEM instrument. The irregular surface shape and some pores were observed on the alginate/pectin-phenanthroline films before Fe(II) sensing (see Fig. 3(a)). This was due to the crosslinking process that did not occur in all polymer chains [17]. After the addition of Fe(II) ion, the film morphology slightly changed in the formation of 1,10-phenanthroline-Fe(II) complexes causing the surface to be more dense and compact (see Fig. 3(b)) [19]. In addition, some agglomerates were observed, indicating the distribution of 1,10-phenanthroline-Fe(II) complexes.
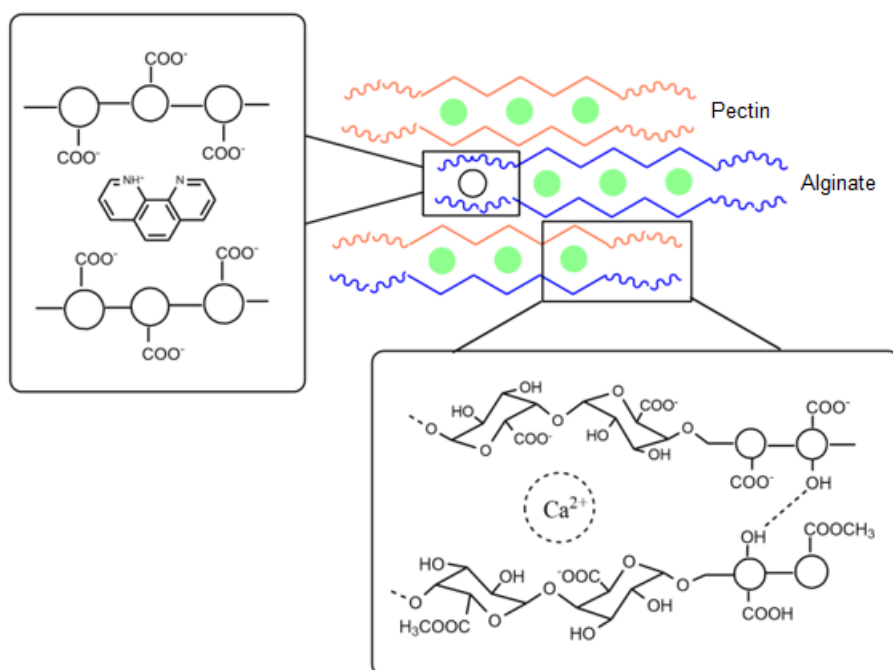
Table 1 shows the results of the SEM-EDS analysis

Fig 2. Proposed interaction between alginate/pectin matrix and 1,10-phenanthroline
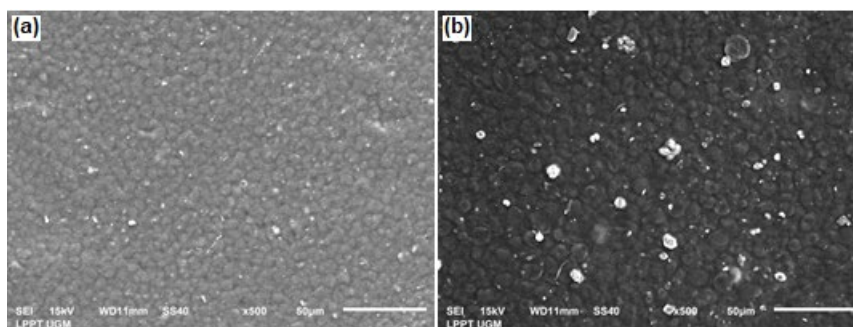
Fig 3. SEM image of alginate/pectin-phenanthroline films (a) before and (b) after sensing with Fe(II) ion

Table 1. Results of EDS analysis of alginate/pectin-phenanthroline films

Before sensing			After sensing		
Element	% Mass	% Atom	Element	% Mass	% Atom
C	34.88	42.64	C	34.78	42.70
O	60.73	55.74	O	60.15	55.44
Ca	4.16	1.53	Ca	5.04	1.85
Cl	0.23	0.10	Fe	0.02	0.01

of alginate/pectin-phenanthroline films before and after the sensing process. The presence of Fe(II) ions can be proven through the data from the EDS (Energy Dispersive X-ray Spectroscopy) analysis. The presence of Fe can be seen in the alginate/pectin-phenanthroline film after the sensing process, even though the amount (% mass) is relatively small (0.02%). The amount of Fe element in the film is very small compared to the amount of C and O elements, which are the key elements of the alginate/pectin film. Other elements such as Ca and Cl contained in the alginate/pectin-phenanthroline film are derived from $CaCl_2$, which acts as a crosslinking agent.

Optimization of the Condition for Fe(II) Ions Detection Using Alginate/Pectin-Phenanthroline Film

The principle of the colorimetric method was based on the formation of a complex between the chromogenic reagent and the analyte. In this study, 1,10-phenanthroline was used as the chromogenic reagent and immobilized in alginate/pectin films, while the analyte was Fe(II) ions. Therefore, when the alginate/pectin-phenanthroline film was contacted with Fe(II) ions, the orange-red color of the complexes formed was observed. Although the formation of phenanthroline-Fe(II) complexes was observed by naked-eye (qualitative

analysis), the UV-Vis spectrophotometer analysis was performed by quantitative measurement. The maximum absorption wavelength of the phenanthroline-Fe(II) complex formed at 513 nm (see Fig. 4) was not significantly different from the previous study found at 510–515 nm [3,20].

It was well known that the nature of the chromogenic reagent and the metal ions depended on the pH of the aqueous system. Therefore, the 1,10-phenanthroline and Fe(II) ions formed a soluble and stable complex in the pH range 2–9 [20-21]. However, at
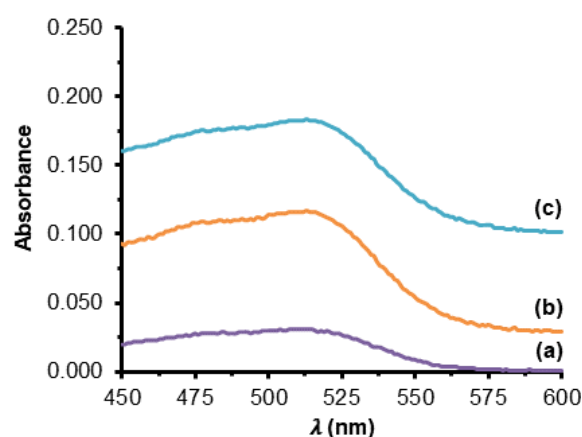

Fig 4. UV-Vis spectra of alginate/pectin-phenanthroline film after the addition of Fe(II) ion at the concentrations of (a) 2, (b) 5, and (c) 10 mg L^{-1}

pH above 4, Fe(II) ion reacted with OH^- to form $Fe(OH)^+$ and the insoluble $Fe(OH)_2$, which blocked the active site of the film, resulting in the decrease of absorbance. Fig. 5 showed that the highest absorbance was achieved at pH 2. At pH 3 and 4, the amount of protonated 1,10-phenanthroline is less than at pH 2. The unprotonated form of 1,10-phenanthroline tends to leach into the solution and react with free Fe(II) ions forming $[Fe(II)(phen)_3]^{2+}$ in the solution. This phenomenon causes a decrease in the absorbance of the alginate/pectin film. However, at a very strong acidic solution (pH = 1), the amount of H^+ in the solution is huge compared to the amount of Fe(II) ions, thus lowering the affinity of the 1,10-phenanthroline present in the film to react with Fe(II) ions.

The optimum concentration (in wt/v) of 1,10-phenanthroline was determined by varying the solution in the alginate/pectin films. Meanwhile, the films' capacity depended on the number of carboxyl groups (anions) that interacted with phenanthroline. Fig. 6 showed that the highest absorbance of the films was found in 0.2% 1,10-phenanthroline. This indicated that there were still negative charges in the alginate/pectin film, which have not bound for the optimal formation of complexes between Fe(II) ion and phenanthroline. This absorbance reached a plateau at a concentration of 0.2–0.3% since all the negative charges of alginate/pectin have been bound to 1,10-phenanthroline. The effect of the sensing method was also studied by the varying contact time between 0 to 2 min. The result showed that 2 min was sufficient to give a measurable absorbance of the color changes in alginate/pectin-phenanthroline films (see Fig. 7). This indicated that the films were suitable as a rapid optical sensor agent for Fe(II) detection.

Interference Study of Fe(II) Ions Detection in the Presence of Other Metal Ions

The main purpose of preparing the alginate/pectin-phenanthroline film as the optical sensor was to detect Fe(II) ions in environmental samples, especially on surface water. Therefore, some of the interference of metal ions that were present in the water samples became very important to be considered. This was due to the other metal ions that also reacted with 1,10-phenanthroline, lowering its ability

to bind Fe(II) ions. This study was carried out using three different concentrations (5, 10, and 20 mg L^{-1}) of
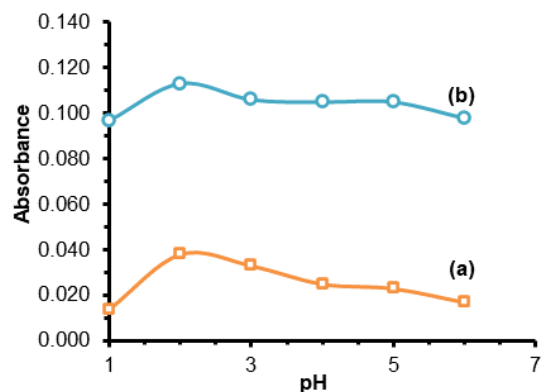

Fig 5. The effect of pH solution on the absorbance of alginate/pectin-phenanthroline films when the Fe(II) concentrations were (a) 2 and (b) 8 mg L^{-1}
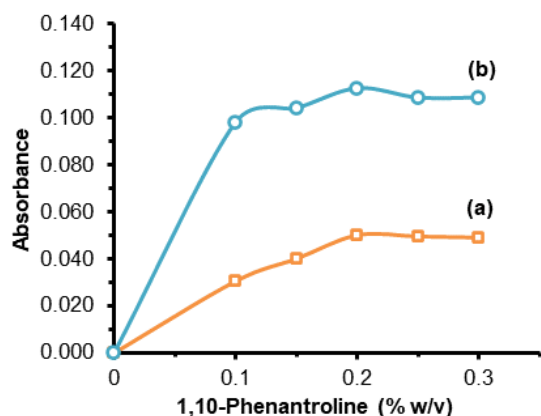

Fig 6. The influence of 1,10-phenanthroline concentration on the absorbance of alginate/pectin-phenanthroline films, when the used Fe(II) concentration was (a) 2 and (b) 8 mg L^{-1}
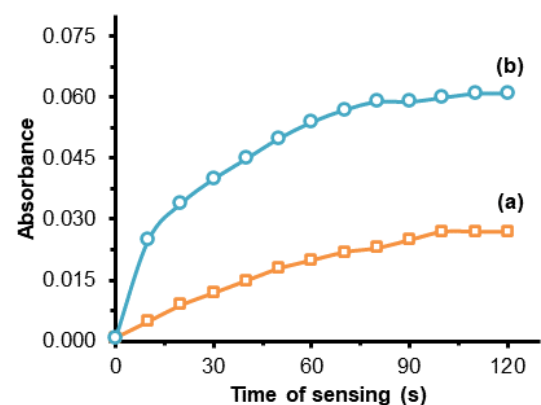

Fig 7. Optimization time of sensing when the used Fe(II) concentration was (a) 2 and (b) 4 mg L^{-1}

interference ions, such as Pb(II), Ni(II), Fe(III), Cu(II), Zn(II), Co(II), Mg(II), and Ca(II), in 25 mL solution while Fe(II) was fixed at 5 mg L^{-1}. As shown in Fig. 8, the addition of various interference metal ions except for Fe(III) ion. It did not significantly influence the Fe(II) ions detection using alginate/pectin-phenanthroline film. Even though some metal ions existed at 4 times higher concentration than Fe(II) ions, the absorbance value of the films tends to be constant, demonstrating a good selectivity for Fe(II) detection. However, Fe(III) ions influence the Fe(II) detection due to their similar cationic

size and physicochemical properties. To overcome this problem, the Fe(III) ions were reduced first using hydroxylamine hydrochloride at pH 2 solution. Therefore, the total Fe ions concentration at the environmental samples was measured.

Calibration Curve and Sensitivity of Alginate/ Pectin-Phenanthroline Film for Fe(II) Quantification

Using the optimum condition for Fe(II) detection (i.e., 2 min contact time at pH 2 solution with 0.2% wt/v of 1,10-phenanthroline), a linear calibration curve with
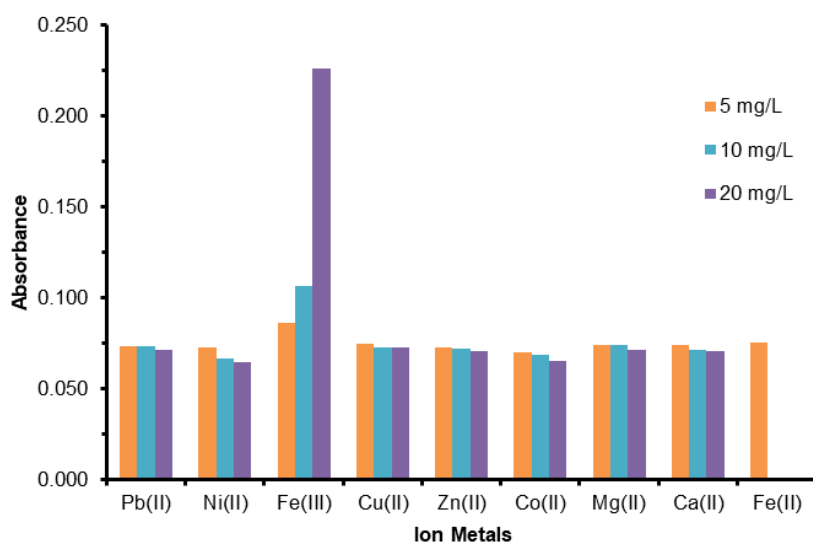

Fig 8. The colorimetric response of alginate/pectin-phenanthroline films in various concentrations of interference metal solution (5, 10, and 20 mg L^{-1}). The concentration of Fe(II) ion was fixed at 5 mg L^{-1} in all solutions
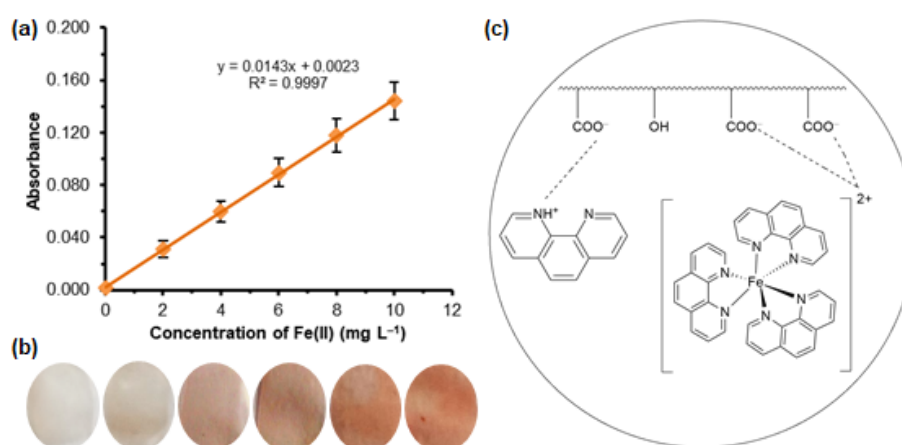

Fig 9. (a) Calibration curve of alginate/pectin-phenanthroline films at various Fe(II) concentrations, (b) the corresponding color of the alginate/pectin-phenanthroline films. From left to right, the concentration of Fe(II) solution was 0, 2, 4, 6, 8, and 10 mg L^{-1}, respectively, and (c) proposed interaction between alginate/pectin matrix and [Fe(II)(phen)$_3$]$^{2+}$

high R^2 (0.997) in the range concentration of Fe(II) 0–10 mg L^{-1} was obtained (Fig. 9(a)). The corresponding color of the alginate/pectin-phenanthroline films and proposed interaction between alginate/pectin matrix and $[Fe(II)(phen)_3]^{2+}$ are shown in Fig. 9(b) and (c), respectively. The limit of detection for Fe(II) ions (0.446 mg L^{-1}) was remarkable. The precision of the quantification method was evaluated by testing the repeatability of the sensor films. The colorimetric response of the films was measured with 3 repetition tests in 3 different batches. Based on the statistical method, the relative standard deviation (RSD) of the different batches were range from 0.70–3.13%, indicating good precision of the proposed method.

Detection of Fe(II) Ions in the Tap Water Sample Using Alginate/Pectin-Phenanthroline Film

The applicability of the film sensor was performed by determining the Fe(II) concentration in the tap water sample. Tap water samples were analyzed using atomic absorption spectrometry, resulting in concentrations of Ca, Fe, Mg, K, and Na ions of 7.0, 0.04, 4.9, 9.5, 63.1 ppm, respectively. The sample was spiked with Fe(II) standard solution at 2, 5, and 10 mg L^{-1}, then measured using a UV-Vis spectrophotometer in optimum condition. Table 2 showed that the films sensor had good % recoveries between 102.10–110.72%, indicating a good accuracy for Fe(II) detection. The range of % recoveries value obtained was in accordance with that of the sample category in ppm

units, between 80–110% [22]. This showed that the presence of other disruptive matrices or other interferent metal ions in the tap water sample did not affect the detection of Fe(II) ions using alginate/pectin-phenanthroline films. However, there was a possibility that Fe(III) ions were contained in the tap water sample and might affect the detection of Fe(II). To overcome this problem, the tap water sample needed to be treated with hydroxylamine hydrochloride, causing the total Fe ions in the tap water sample to be in the form of Fe(II) ions for its detection to be optimal.

In addition, we have also compared the performance of the present sensor film with the other sensors available in the literature (Table 3). It can be seen that the detection of Fe(II) using alginate/pectin-phenanthroline film is promising to be an alternative method of Fe(II) in the water sample. Alginate/pectin film could be easily degraded in the environment. It makes this research has more advantage than other sensors. In addition, the complicated stages of reagent

Table 2. Determination of Fe(II) ion concentration in tap water sample using alginate/pectin-phenanthroline film in the optimum condition

Fe(II) added (mg L^{-1})	Fe(II) (mg L^{-1})	% recovery
0	0.469	-
2	2.683	110.72
5	5.667	103.96
10	10.678	102.10

Table 3. Comparison of performance of different Fe sensors with the presence sensor

Analyte	Method	Medium	LOD (mg L^{-1})	Ref.
Fe(II)	Potentiometric determination	Solid probe (2, 6-bis (carboxamide methyl ester) pyridine derivative as neutral ionophore in plasticized PVC membrane)	0.224	[9]
Fe(II)	UV–Vis absorption of Fe–2-(2-pyridyl) imidazole complex	Solid probe (2-(2-pyridyl)imidazole functionalize poly(vinylbenzyl chloride) (PVBC) nanofibers made into membrane)	2.0	[23]
Fe(III)	Naked eye observation	Solid Probe (Curcumin loaded in Zein membrane)	0.40	[24]
Fe(II & III)	UV-Vis absorption of Fe−1,10-phenanthroline complex	Solid probe (1,10-phenantrhroline entrapped in poly(acrylamide) membrane)	0.02	[3]
Fe(II)	UV-Vis absorption of Fe−1,10-phenanthroline complex	Solid probe (1,10-phenanthroline entrapped in alginate/pectin film)	0.446	Present work

syntheses did not require for this study. The 1,10-phenanthroline reagents can be obtained easily and react very selectively with Fe(II) ion compared to other metal ions.

■ **CONCLUSION**

The alginate/pectin-phenanthroline film optical sensors were successfully prepared by immobilizing 1,10-phenanthroline in alginate/pectin films. The optimum condition for Fe(II) detection was obtained at pH 2 for 2 min contact time and 0.2% of 1,10-phenanthroline concentration. The alginate/pectin-phenanthroline provided high accuracy, precision, and selectivity for Fe(II) in the aquatic environmental samples, with a detection limit of 0.446 mg L^{-1}. Therefore, the alginate/pectin-phenanthroline film optical sensor was found as a simple, fast, accurate, and alternative method for Fe(II) ions detection in the environmental samples for routine daily analysis.

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