UV–Visible Spectroscopy for Kinetic Study of Fluorescein-Labeled Starch Adsorption at Ferric Chloride

Fateh Eltaboni and Abdelqader Imragaa

Department of Chemistry, University of Benghazi, Benghazi, Libya.

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ABSTRACT

Fluorescein 5(6)-isothiocyanate-starch (FITC-S) biopolymer was prepared via covalently attached fluorescein 5(6)-isothiocyanate (FITC) with starch. FITC-S with an average molecular weight length of 3×10^6 g/mol was formed upon precipitation in alcoholic solution. FITC-S showed absorption maxima at around 490 nm in aqueous medium. The adsorption of the photoactive starch onto ferric chloride ($FeCl_3$) was studied using UV–visible spectroscopy. Spectra of the adsorbed biopolymer were collected as a function of time and as a function of concentration. Measurement of the peak intensities of the adsorbed FITC-S allowed adsorption isotherms and adsorption kinetics to be determined for biopolymer at different pH values. Unmodified Langmuir fitting for experimental data yielded a Gibbs free energy of adsorption (ΔG_{ads}^{o}) at pH 7, pH 9, and pH 11 of -55, -52and -51 kJ/mol, respectively, which correlate well with similar values determined modified Langmuir model. Kinetic analysis indicated that the adsorption of FITC-S was a pseudo-first-order process over pH range studied. Furthermore, the adsorption lifetime (τ_{ad}) was decreased to 46 min by decreasing the pH to 6.5., as the electrostatic attraction between starch and the oppositely charged ferric chloride was enhanced.

INTRODUCTION

A chromophore, also known as photo-active probe, can be defined as a molecule, which absorbs energy of a specific wavelength. The intensity and wavelength of the absorbed photon depend on both the chromophore and its surrounding environment[1]. Despite incorporation chromophore molecules into macromolecules can be simply done by dissolving the chromophore[2, 3], this type of probing suffers from several major setbacks such as possible leakage of chromophore that subsequently leads to toxicity of the aqueous system and incorrect signal measurements[2, 4]. In order to overcome these problems, we previously managed a successful covalent chromophores attachment onto polymer molecules [5, 6]. Covalent attachment is proven to reduce the leakage of chromophore, provide good photostability, and produce stable signals[2]. Since the starch is weak photo-active polymer, in this work, we have successfully synthesized fluorescein 5(6)-isothiocyanate-starch (FITC-S) in order to monitor the adsorption behavior of the starch at liquid-solid interface. One main benefit of utilizing fluorescein is that it can be covalently attached in suitably tiny quantities so that they do not disturb the conformational behavior of polymer[7]. The second advantage is that the photo-response of the covalently attached fluorescein label can be directly related back to the polymer itself [8].

Ferric chloride is a coagulant material causes turbidity and color of drinking water[9]. The adsorption of polysaccharides like starch onto ferric chloride is efficient in water turbidity removal[9]. For charged polysaccharides, mainly strong electrostatic interaction controls their adsorption onto minerals, whereas, H-bonding and solvation forces play vital role in uncharged polysaccharides adsorption [10-12]. Although many studies [10-14] have reported that the adsorption behavior of starch onto minerals is mainly governed by parameters like solution pH and concentration, still the molecular interactions of an adsorbed starch are not completely understood. However, it is well known that starch chain expands at pH higher than its pKa value (pKa = 12.6[15]), due to electrostatic repulsion between ionized starch hydroxyl groups [15, 16]. In addition, the starch hydroxyl groups may interact with mineral surfaces via weak hydrogen bonding or strong chemical interaction[12]. The stability of adsorbed polysaccharides at solid surfaces is controlled by the conformation adopted by their chains [14].

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Expanding upon previous work, we deliver an insight into the adsorption behavior of naturally occurring starch onto mineral surfaces[6]. In this work, we present adsorption data for fluorescein 5(6)-isothiocyanate-starch onto ferric chloride. The effect of the hydroxyl ionization in starch chain on the adsorption capacity was investigated. Adsorption and kinetic isotherms were determined by UV–visible spectroscopy.

MATERIALS AND METHODS

Experimental Section

Material

The MERCK ferric chloride ($FeCl_3.6H_2O$) as coagulant with a particle diameter of 60 ± 1.4 nm, surface area of 355 m^2/g was purchased from Sigma-Aldrich, UK, starch (from Riedel-De Haenag Seelze- Hannover) was used as coagulant aid, fluorescein isothiocyanate isomer I chromophore (FITC, Sigma-Aldrich, UK), hydrochloric acid and sodium hydroxide (0.1N, Sigma-Aldrich, UK) were used for pH adjustment, anhydrous tetrahydrofuran (THF, Sigma-Aldrich, UK), propanol (Sigma-Aldrich, UK). The experiments were performed in high purity water (18 $\Omega^{-1}cm^{-1}$).

Labeling Reaction

Fluorescein 5(6)-isothiocyanate-starch (FITC-S) was prepared based on method adapted from Cho *et al.* [17], with slight modification, see Figure 1. 10 mg of FITC and 5 g of starch were dissolved in 35 mL of anhydrous THF. The reaction was carried out at room temperature for 1 hour. The viscosity-average molecular weight M_v of pure starch and labeled-starch, with low loading of the anthracene (0.1 mol%), were determined to be 3.5 x10^6 and 3 x 10^6 g/mol using viscometry, values of 0.59 and 0.29 for *K* and *a*, respectively, in water at 25°C [18].

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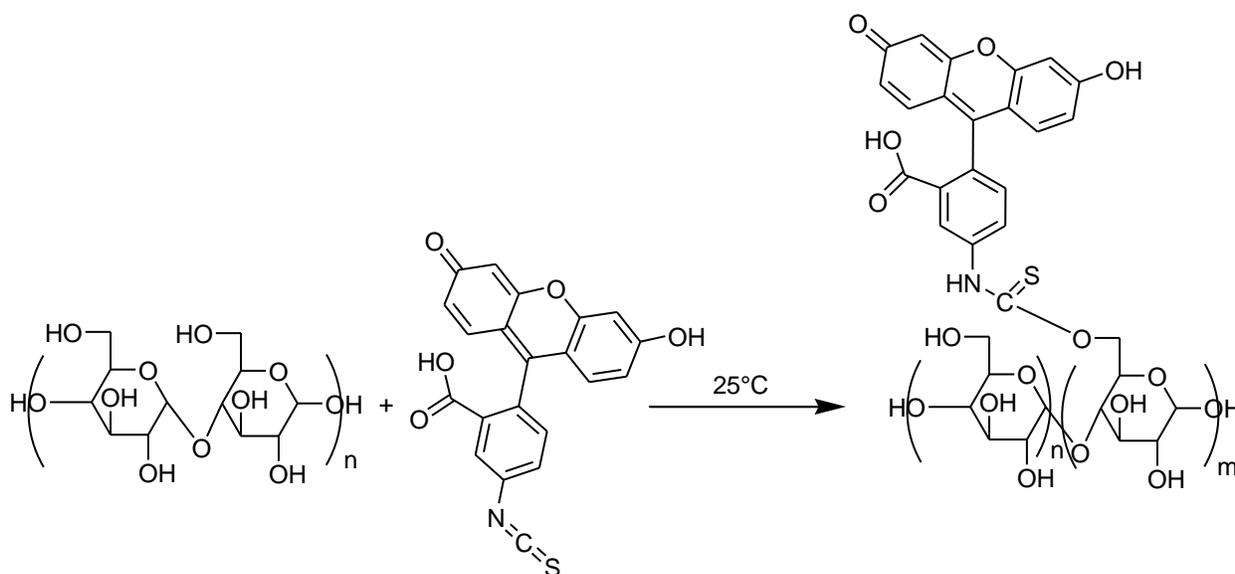
Figure 1. Labeling reaction of starch with FITC

Degree of Labeling

To estimate the quantity of chromophore label ($[mol\%]_{FITC}$) in the starch, ultraviolet (UV) spectra were recorded with a Perkin–Elmer spectrophotometer. The scan was done from 600 nm to 200 nm with a scan speed of 400 nm/min. Free chromophores were measured at different concentrations in methanol spectroscopic grade, whereas polymer solutions at 10^{-1}wt% in deionized water were prepared and measured at room temperature. The mol % of the chromophore label was calculated by the following equation:

$$[mol\%]_{FITC} = \frac{c_{FITC}}{c_{FITC} + c_{Monomer}} x\ 100 \quad (1)$$

Where, C_{FITC} and $C_{Monomer}$ are the molar concentration of the chromophore label and the starch monomer, respectively.

Adsorption Experiment

The exact proportions of FITC-S and 10 mg of $FeCl_3$ were mixed, and then the pH adjusted to the necessary value. The mixture was shaken overnight to ensure that adsorption had reached equilibrium. The solution was then left for 6 hours to deposit the solid phase from the aqueous phase. The supernatant was then carefully withdrawn from the top of the sample tube. To quantify the amount of adsorption, ultraviolet (UV) spectra were recorded with a Perkin–Elmer

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spectrophotometer of FITC-S mineral solution before and after separation. The scan was done from 200 nm to 600 nm with a scan speed of 400 nm/min. The adsorbed amount was calculated by the difference in the absorbance of FITC-S solutions before and at adsorption by the Beer-Lambert law (maximum absorption intensity at 490 nm). Absorption intensities were expressed in arbitrary units (a.u).

Kinetic Experiment

The correct proportions of FITC-S were measured and mixed with 10 mg $FeCl_3$, and then the pH of the sample adjusted to the required value, immediately absorbance at 490 nm, which is characteristic for FITC chromophore, was recorded as a function of time and directly obtained in the form of a graph. This graph was fitted to an exponential function; hence the adsorption lifetime was determined.

RESULTS AND DISCUSSION

Spectroscopy characterization of synthesized FITC-S polymer

The labeling reaction of the native starch occurred via a covalent binding between the isothiocyanate group of FITC chromophore and the OH group of starch as shown by the scheme in Figure 1. The degree of labeling ($[mol\%]_{FITC}$) of starch was found to be 0.50, which is small enough and does not disturb the conformational behavior of starch. The UV/Vis absorption spectra of starch and FITC-S in water at pH 7 were displayed in Figure 2. FITC-S showed an intensive absorption maximum at around 490 nm, this FITC distinguishing peak was not observed in the unlabeled starch. This new peak suggested that the starch backbone was successfully attached with FITC during the labeling reaction. Accordingly, the adsorption and kinetic behavior of the photo-active starch onto ferric chloride were carried out.

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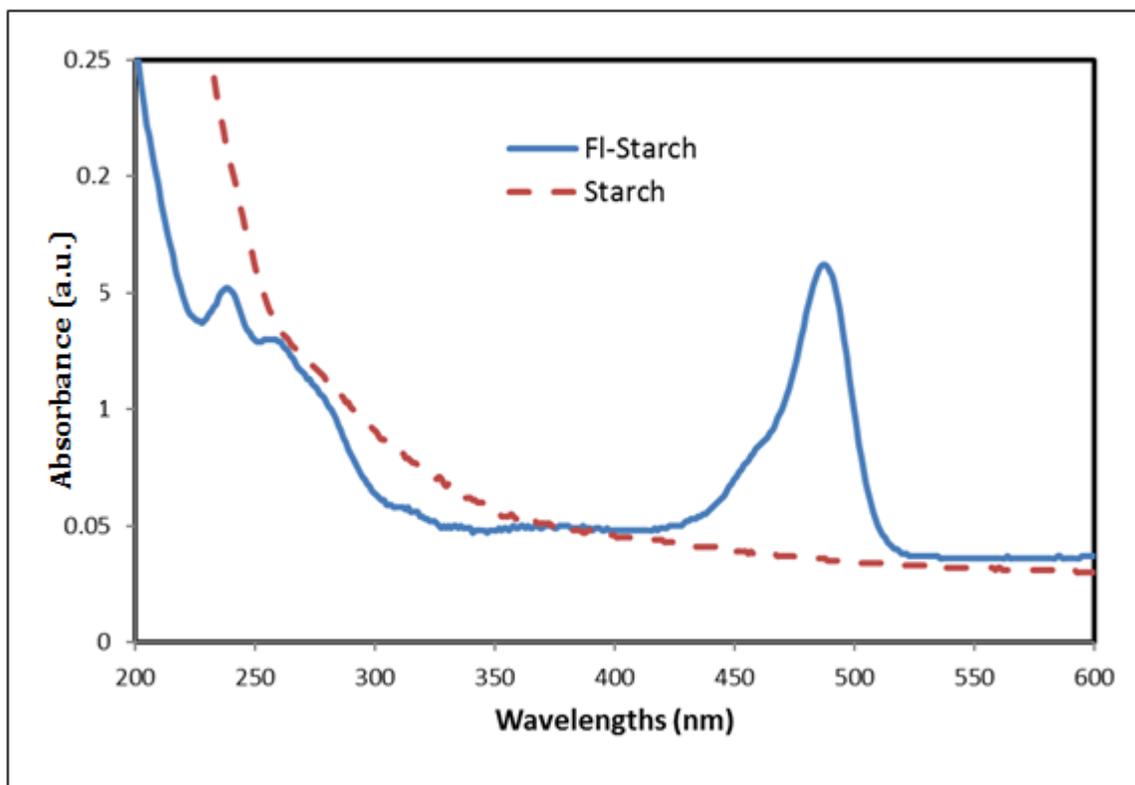
Figure 2. UV/Vis **Absorption spectra of FITC-S in aqueous solution (—) and starch (- -), the concentration of prepared polymers was 1 mg/10 mL at pH 7 and 25 ^{o}C.**

Adsorption isotherms of FITC-S adsorption

The adsorption of chromophore covalently attached to starch onto solid is accompanied by changes in the absorbance of the polymer solution [6]. Since adhesion of this photo-active polymer onto mineral surface led to settling down of the polymer chains, as a result the polymer concentration decreases in the bulk solution, thus the absorbance of the supernatant solution will be quenched as stated by the well-known Beer-Lambert law[19]. A versatile technique like UV–visible spectroscopy, which monitors photo-active polymer absorbance, should be useful for investigating macromolecule-surface adsorption isotherms. Adsorption of the FITC-S onto the ferric chloride surface was indicated by the decrease in the spectral peak intensity that would not otherwise be observed without an interaction between the polysaccharide and mineral. Decrease the absorbance at adsorption demonstrating that the amount of FITC-S at the FeCl$_3$ surface increases. Figure 3 shows the UV/Vis absorption spectra of FITC-S aqueous solutions before and at the adsorption onto FeCl$_3$ as a function of pH. As it can be seen, a dramatic decrease in the

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absorbance of the adsorbed starch was recorded at pH 7. There were otherwise a slight decreasing in the absorbance with increasing the pH of the solution towards 9 and 11. The pH dependence of the adsorption was attributed to the starch and mineral point of zero charges (pH$_{pzc}$)[6]. pH$_{pzc}$ is 9 for starch and 6 for ferric chloride. It means that the ferric chloride particles always bear a negative charge in this study, while the starch is negatively charged at pH 11, neutral at pH 9 and positively charged at pH 7. Consequently, strong electrostatic attraction between FITC-S chains and the FeCl$_3$ suspensions is more favorable to occur at pH 7, indicated by a decrease in the absorbance. When the starch and mineral are negatively (i.e. at pH 11), the adsorption of starch on the ferric chloride suspensions may be because of that hydrophobic forces appear between starch and the mineral particles. Otherwise, the interaction of similarly charged materials should not occur[20]. At pH 9 besides the hydrophobic forces, the hydrogen bonding could play role in the adsorption.
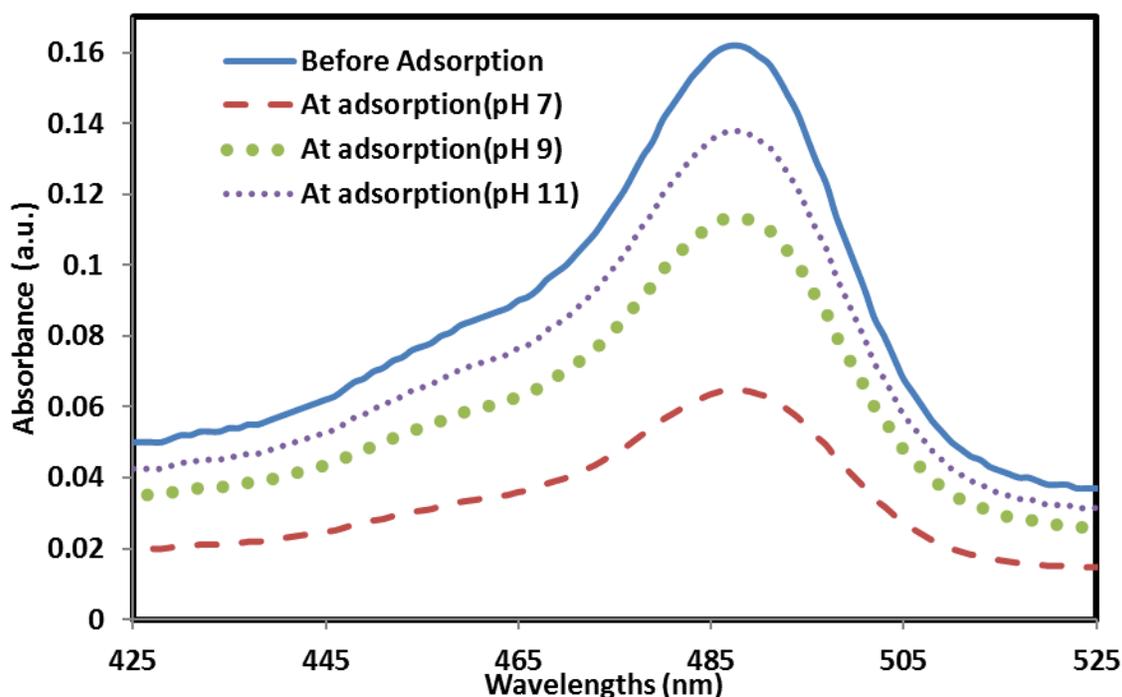
Figure 3. UV/Vis absorption spectra of aqueous FITC-S (1mg/10 mL) and FeCl$_3$ solutions before and at the adsorption state at different pH values.

Adsorption was monitored by observing the absorbance of the FITC-S peak at 490 nm as a function of polymer initial concentration (Figure 5). According to the Beer–Lambert Law, absorbance is directly proportional to concentration and consequently, represents the

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concentration of the adsorbed polymer. The adsorption experimental data was fitted to the modified Langmuir adsorption model [21, 22].

$$\frac{C_i}{A_{diff}} = \frac{C_i}{A_{max}} + \frac{1}{A_{max}K_L} \quad (2),$$

Where C_i is the initial FITC-S concentration (mol/L), A_{diff} is difference in the absorbance of FITC-S at 490 nm before and at adsorption, A_{max} is the maximum absorbance of the 490 nm peak at the isotherm plateau, and K_L is the Langmuir affinity constant. Although the limitation of using Langmuir model for polymer adsorption [22], the parameters gained from the adsorption isotherm fitting made considerable comparisons between the three pH values of adsorbed polymers. The UV–visible absorbance adsorption isotherms (see Figure 5) show that at pH 7 the plateau adsorption reaches its maximum value at absorbance equal to about 0.12, at the pH 9 isotherm the plateau decline to ~0.09 then decreases to ~0.06 at pH 11.

The adsorption of the polymer from bulk solution onto a solid–liquid interface could be explained by the equilibrium displayed in Figure 4 [22],

Polymer (solution) + Water(surface) ⇔ **Polymer (surface) + Water(solution)**
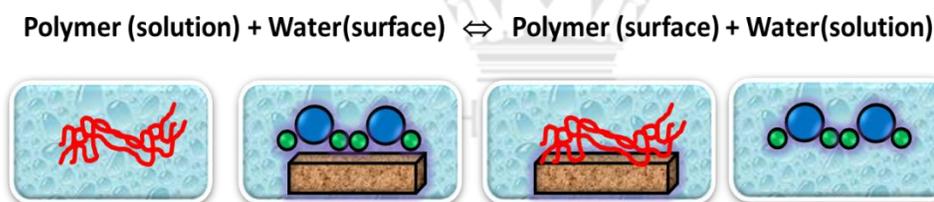
Figure 4. The mechanism of polymer adsorption at a solid–liquid interface

The equilibrium constant of this adsorption (K_{ad}), is derived from the affinity constant (K_L) by using Equation (3) [22]

$$K_{ad} = K_L x\, 55.5 \quad (3),$$

Where, the value 55.5 relates to the molar concentration of water (mol/L) for dilute solutions. The Gibbs free energy of adsorption (ΔG^o_{ads}) of the starch adsorption onto the ferric chloride surfaces can be calculated using the K_{ad} value obtained from the equation (3), see Equation (4) below. The negative values for ΔG^o_{ads} indicates a favourable binding of starch to the FeCl$_3$ surface,

$$\Delta G^o_{ads} = -RTLnK_{ad} \,(4),$$

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Where, R is the gas constant (8.31451 J/ K mol) and T is the temperature in Kelvin scale (K)
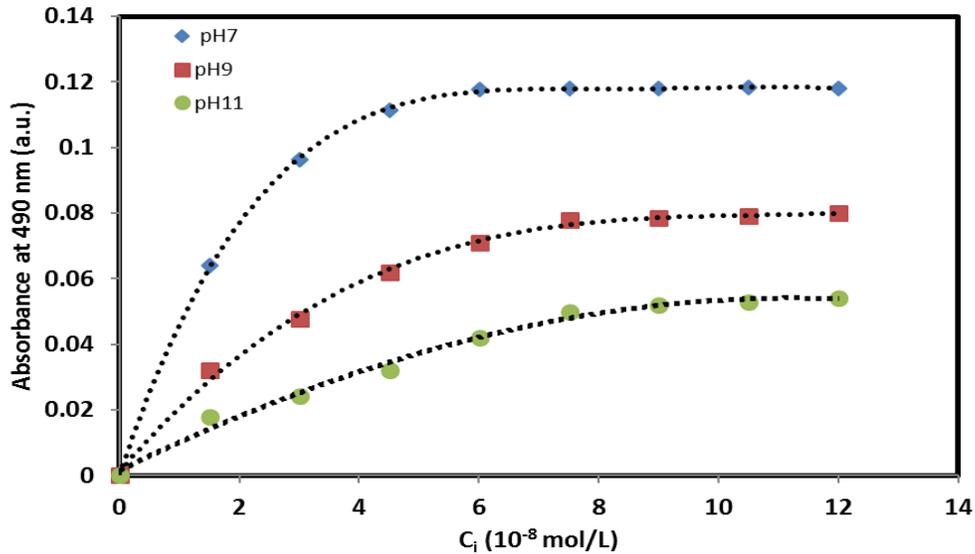
Figure 5. Adsorption isotherms of FITC-S onto ferric chloride at different pH values in aqueous solution as a function of the initial starch concentration, isotherms based on absorbance. The points (●, ■, ▲) are the experimental data, while the dotted lines (…) are the mathematical fitting by modified Langmuir model.
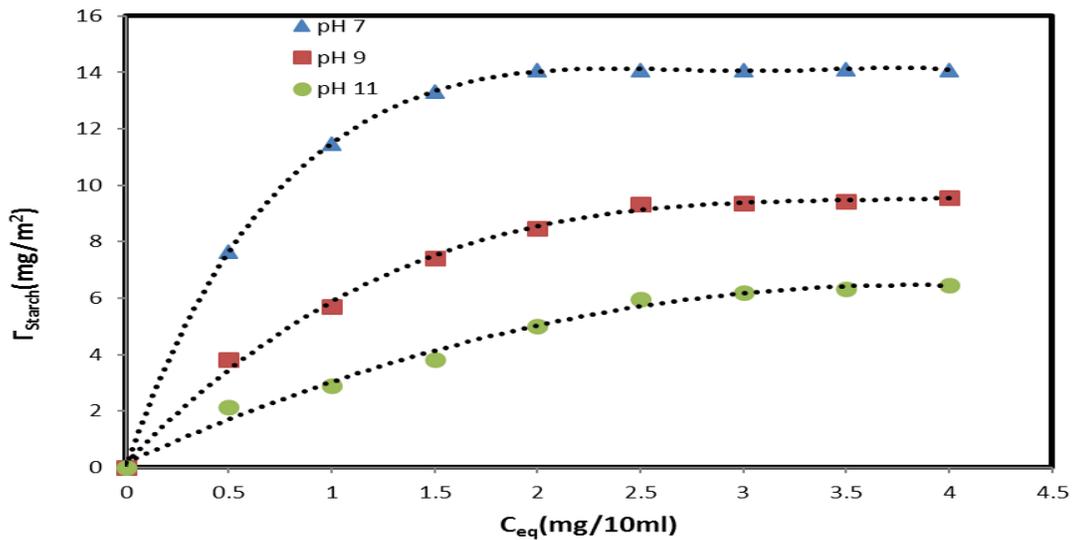
Figure 6. Adsorption isotherms of FITC-S onto ferric chloride at different pH values in aqueous solution as a function of the equilibrium starch concentration, isotherms quantified using steady UV/Vis spectroscopy. The points (●, ■, ▲) are the experimental

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data, while the dotted lines (…) are the mathematical fitting by unmodified Langmuir model.

The K_{ad} values obtained for FITC-S at different pH values suggest that the polymer has a markedly higher affinity for the ferric chloride surface at pH 7 than pH 9 and pH 11. The higher K_{ad} value for FITC-S adsorption at pH 7 may, therefore, be due to the electrostatic interaction onto the mineral.

To compare the values of the equilibrium constant and the standard free energy of adsorption obtained from the modified Langmuir model. The adsorbed amount adsorption isotherms were determined by plotting the adsorbed amount (Γ, mg /m^2) as a function of the equilibrium polymer concentration (C_{eq} ,mg/10 mL) as displayed in Figure 6. The experimental data was fitted to the unmodified Langmuir model [22] (Equation (5), where Γ_{max} is the maximum adsorbed amount (mg/m^2) and K_L is the Langmuir affinity constant described before.

$$\frac{C_{eq}}{\Gamma} = \frac{C_{eq}}{\Gamma_{max}} + \frac{1}{\Gamma_{max}K_L} \quad (5)$$

Since Γ is calculated from Equation (6)

$$\Gamma = \frac{(C_i - C_{eq})V}{mA} \quad (6),$$

Where, C_i initial polymer concentration (mg/mL), C_{eq} is the equilibrium polymer concentration (mg/mL), V is the volume of sample (mL), m is the mass of FeCl$_3$ (mg), and A is the specific area of FeCl$_3$ (m^2/mg). ΔG_{ads}^o and K_{ad} were estimated in the same way as for the modified Langmuir adsorption isotherm data. These calculated thermodynamic parameters are listed combined in Table 1. Both adsorption isotherm plots (Figures 5 and 6) are of the high affinity type with a gradual rise at the start of adsorption and a plateau that is indicative of Langmuir isotherm behaviour. It was assumed that [22] the rounded shape in the initial rise in the isotherm is because of the replacement of low molecular weight chains with high molecular weight chains until equilibrium is reached and reflects the polydispersity of the polymer samples. The values of K_{ad} and ΔG_{ads}^o gained from the unmodified Langmuir model are comparable with those obtained by the modified Langmuir expression. The advantage of unmodified Langmuir model is that a quantified adsorbed amount of FITC-S can be used to predict the mass of polymer adsorbed per

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unit area of ferric chloride surface. Otherwise, the modified Langmuir model is easily achievable via monitoring the absorbance of FITC-S.

Table 1. Calculated parameters obtained by fitting adsorption isotherms to the modified and unmodified Langmuir model for FITC-S adsorption onto FeCl₃.

pH	Modified Langmuir adsorption model					Unmodified Langmuir adsorption model				
	A_{max} (a.u.)	$K_L x10^8$ (L/mol)	R^2	K_{ad} $x10^8$	ΔG^o_{ads} (kJ/mol)	Γ_{max} (mg /m²)	$K_L x10^8$ (L/mol)	R^2	K_{ad} $x10^8$	ΔG^o_{ads} (kJ/mol)
11	0.06	0.3	0.87	16	-52	10	0.2	94	9	-51
9	0.09	0.5	0.96	30	-54	12	0.3	98	15	-52
7	0.12	1.6	0.99	88	-57	16	1.0	99	51	-55

A good agreement was observed between experimental and simulated results, as it can be noticed the parameters in Table 1 show that the absorbance and adsorption density reach to their maximum values (0.12 and 16 mg/m²) when the pH of solution decreased from 11 to 7. Despite the little difference between in values of K_L and K_{ad} generated modified and unmodified Langmuir model, both were increased by increasing the pH, which means that the starch chain has a greater affinity at low pH than at higher pH values. The free energies of adsorption obtained by modified Langmuir are in closer agreement with unmodified, in addition. As the pH decreases to 7, the net charge on starch becomes partially positive which provides an electrostatic attraction to the anionic ferric chloride particles.

Kinetics study of FITC-S adsorption

The adsorption lifetime was determined using the UV–visible spectroscopy technique. The FITC-S concentration selected for these experiments was 3 mg/mL, corresponding to the beginning of the plateau of adsorption isotherm experiments. Figure 7 displays the absorbance intensity for the adsorption of FITC-S onto FeCl₃ at 490 nm as a function of time in seconds scale. A pseudo-first-order rate equation [22] was used to fit the kinetic data, hence the adsorption lifetime (τ_{ad}) was generated:

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$$A_t = A_{max}\left(1 - e^{-\frac{t}{\tau_{ad}}}\right) \quad (4)$$

Where A_t is the absorbance as a function of time t at 490 nm, A_{max} is the maximum absorbance at 490 nm and t is the time in seconds. Kinetic plots for FITC-S adsorption (at pH 7 and pH 11) are displayed in Figure 7 combined with the fitted curves derived from Equation (4). The results in Figure 7 shows that the pseudo-first order model describes well the experimental data as its corresponding R^2 value is considerably high (between 0.997 and 0.998). The absorbance decay of the polymer in the presence of ferric chloride was found to be pH dependent. It was found that the maximum absorbance of 0.5629 decays until reaching a plateau of 0.1194 after 52 minutes at pH 11, whereas at pH 7 the absorbance decays rapidly from 0.5526 to 0.07064 after 46 minutes. Probably, the increase in the amount of adsorbed starch at lower pH causes a decrease in maximum absorbance and adsorption lifetime values. Since the stronger interaction between the FITC-S and FeCl$_3$ at pH 7 is followed by a marked decrease in FITC-S in solution.
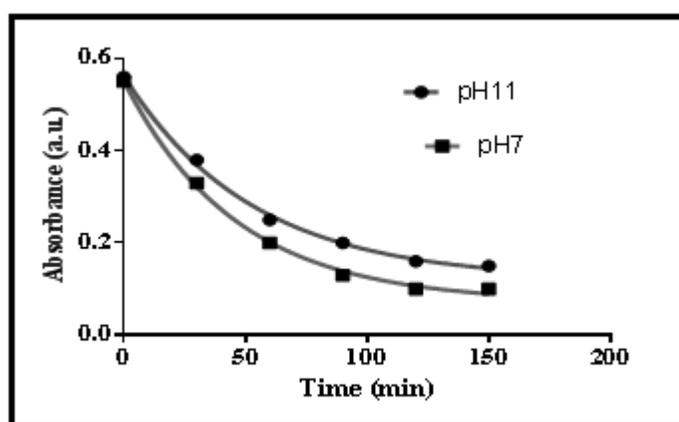
Figure 7. Kinetic plots for FITC-S adsorption onto ferric chloride determined by UV–visible spectroscopy. (At 25 °C and 1 mg/ mL polymer), (●) experimental at pH 11, (▪) experimental at pH 7, and (—) pseudo-first-order model (R^2 = 0.997 at pH 11 and R^2 = 0.998 at pH 7). (Data represent mean values of triplicate measurements).

Figure 8 displays adsorption lifetimes (τ_{ad}) of FITC-S as a function of pH, indicating the pH dependence of τ_{ad} for starch adsorption onto mineral surface. As can be seen, the maximum adsorption lifetime (52 min) has been observed at pH 11. While, between pH 6.5 and 8 the τ_{ad} decreases from 48 min to 46 min, this suggests that within this range there is a strong adsorption of positively charged FITC-S ions on the oppositely charged FeCl$_3$ surface. At high pH

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conditions (above pH 9) biopolymer and mineral are similarly charged, hence an electrostatic repulsion occurs, this encourages the FITC-S chains to remain in the bulk solution, as a result the adsorption lifetime increase. It is very important to note that the pH dependence of the adsorption lifetime is clearly similar to the fluorescence correlation time □ □$_c$) collected by a powerful technique like fluorescence time resolved spectroscopy (TRAMS), which is discussed in more detail in our previous work [5]. It was found that during investigation of synthetic poly (acrylic acid) adsorption at calcite surface decreasing the pH value was accompanied with an increase in the □$_c$ values since motion of the macromolecular chain is restricted as adsorption proceeds and poly (acrylic acid) binds to oppositely charged mineral.
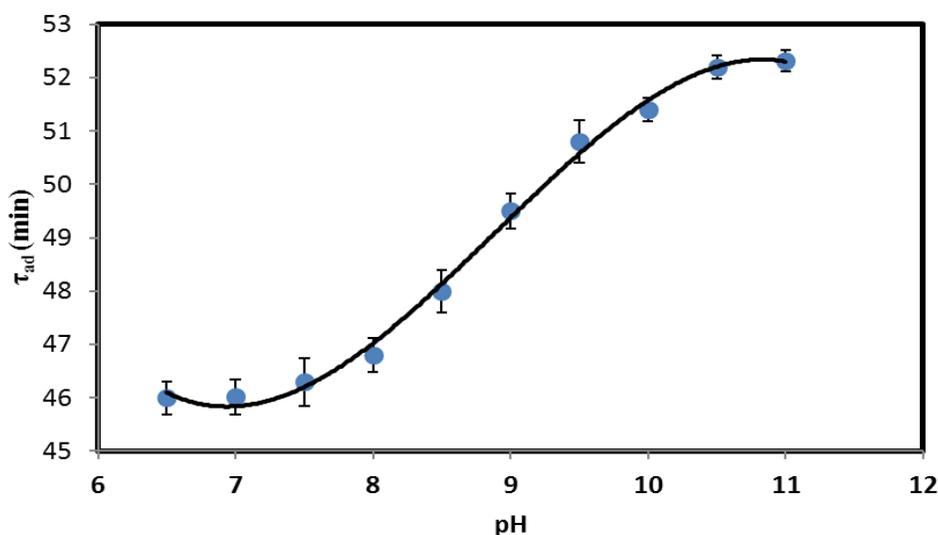
Figure 8. The adsorption lifetimes (□$_{ad}$) for FITC-S ferric chloride mixture as a function of pH. (At 25 °C and 1 mg/ mL polymer), (Data represent mean values of triplicate measurements).

CONCLUSION

The pH study for adsorption of fluorescein 5(6)-isothiocyanate-starch (FITC-S) onto the surface of ferric chloride has been investigated by UV/Vis spectroscopy. Adsorption isotherms were typically fitted by modified and unmodified Langmuir isotherm models. The adsorption constants (K_{ad}), together with the Gibbs free energies of adsorption (ΔG^o_{ads} (indicated that FITC-S has a higher affinity at pH 7 than at higher pH values. This affinity was attributed to that the

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net charge on starch developed partially positive which delivers electrostatic attraction to the anionic ferric chloride surfaces. The modified Langmuir fitting parameters are comparable with those acquired by the unmodified Langmuir model. Adsorption kinetic experiments indicated that the adsorption was a pseudo-first-order process. In addition to variation the absorbance decay upon changing the pH of adsorption, the maximum adsorption lifetime ($\square_{ad}$) has been observed at pH 11. While the minimum $\square_{ad}$ was recorded at pH 6.5, this confirms that at low pH values more FITC-S chains are adsorbed onto the oppositely charged $FeCl_3$ surface.

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