

Article

# Adsorption of Aqueous Iodide on Hexadecyl Pyridinium-Modified Bentonite Investigated Using an Iodine–Starch Complex

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**Abstract:** The sorption affinity of iodide on organo-bentonite, modified with hexadecyl pyridinium (HDPy), was investigated with the iodine–starch method coupled with UV/Vis absorption spectroscopy. The iodine–starch complex method was optimized in terms of the reaction time and sample compositions, based on the UV/Vis absorbance. The batch sorption experiment for iodide on organo-bentonites, modified using two different loading amounts of HDPy, was conducted to analyze the influence of equilibrium time, liquid-to-solid ratio, and temperature, on the iodide sorption affinity. The experimental results regarding the removal capacity were further employed to derive the distribution coefficients of iodide on the organo-bentonites. The novelty of this work lies in the first application of the iodine–starch method coupled with UV/Vis absorption spectroscopy for analyzing the sorption behavior of iodide on modified bentonites. It is expected that the iodide-starch method can be complementarily employed for future research, with respect to the quantification of iodide.

**Keywords:** bentonite modification; colorimetry; decontamination; HDPy; iodide; sorption



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## 1. Introduction

Radioactive iodine-129 is considered to be one of the critical radionuclides contained in nuclear waste due to its long half-life ( $1.57 \times 10^7$  years), high solubility, and considerably low sorption affinity to natural mineral surfaces [1,2]. Among various iodine species—mainly the two different chemical species, iodide ( $I^-$ ) and iodate ( $IO_3^-$ )—are known to be present in the aqueous system [1,3]. Particularly, the aqueous chemistry of iodine is mostly dominated by iodide ions at relatively oxidative and neutral pH conditions (i.e., natural groundwater systems) [3]. Therefore, a precise understanding of the migration and retardation behavior of iodide, based on the reliable quantification analysis method, is one of the key issues related to the safety of nuclear waste disposal.

From the viewpoint of the nuclear waste repository, the compacted bentonite, employed as a buffer material for the retention of radioactive isotopes, provides almost negligible sorption affinity to iodide because of the negatively charged mineral surfaces [4]. However, previous works have shown that the retention capability of bentonite to iodide can be remarkably enhanced by a modification process with various organic cations [4–6] (hexadecyl trimethyl ammonium (HDTMA), hexadecyl pyridinium (HDPy), benzethonium (BE), etc.). Bors et al. [5] reported that the Wyoming bentonite (also known as MX-80), treated with HDPy, provided remarkably high sorption affinity to iodide and pertechnetate ( $TcO_4^-$ ). According to the experimental results, the adsorption capacities of modified bentonites were significantly influenced by the initial HDPy loading of the samples. Subsequently, Rao and Sivachidambaram [4] also confirmed that the organo-bentonites prepared with the HDPy modification process can retain the iodide ions according to the relevant sorption mechanisms, based on the coulombic attraction and anion exchange at primary and secondary sites, respectively. Furthermore, Riebe et al. [6] investigated the anion

adsorption capability of organo-clay minerals modified using various organic cations (i.e., HDTMA, HDPy, BE, etc.), at elevated temperature conditions. The batch experimental data represented significantly high sorption affinities to iodide under both bi-distilled water and synthetic groundwater systems, consistent with the data reported by Bors et al. [5] and Rao and Sivachidambaram [4]. In addition, relative decreases in adsorption rates of iodide with increasing temperatures was identified for all the organic cations investigated. The tendency for iodide sorption to increase along with an increase in the loading amount of organic cations was also observed, consistent with previously reported data [6,7]. In particular, Yang et al. pointed out that the adsorption capacities of modified bentonites were significantly dependent on the HDPy loading of the samples during the modification process, inducing an expansion of the interlayer space of clay minerals [7].

The research works discussed above indicate that the organo-bentonite might be employed as an effective buffer material for nuclear waste repository, providing excellent retention capabilities for various anionic radionuclides. Still, due to the lack of relevant sorption data available for organo-clay minerals in the viewpoint of the geologic repository, further experimental efforts concerning various condition parameters (e.g., liquid-to-solid ratio, temperature, etc.) need to be conducted to optimize the sorption characteristics of modified clay minerals and enhance the safety of radioactive waste disposal.

Various iodide sorption experiments reported to date have employed various quantification analysis methods, such as inductively coupled plasma mass spectrometry (ICP-MS) [7], gamma spectroscopy [5,6], and ion chromatography [4]. However, those quantification methods require either complicated procedures, costly instruments, or radioactive tracers acting as a hindrance to safe and efficient experimental work. In this respect, the UV/Vis absorption spectroscopy [8], based on the iodine–starch complex [9,10], can be alternatively considered as a rapid, easily accessible, and relatively inexpensive quantification method for aqueous iodide.

According to the descriptions above, as a hypothesis, it is expected that (i) the bentonite, modified with an organic cation, can enhance the sorption capacity of bentonite for aqueous iodide, and (ii) UV/Vis absorption spectroscopy can be employed as a simple quantification method for aqueous iodide. In this respect, the objective of the present work is to investigate the sorption behavior of iodide on HDPy-modified bentonite clay minerals by using the iodine–starch method coupled with UV/Vis absorption spectroscopy. The optimized condition for the quantification of iodide was derived based on the UV/Vis absorbance of the iodine–starch complex measured at various reaction times and sample compositions. Furthermore, the sorption affinity of iodide on organo-bentonites was determined at various liquid-to-solid ratios and at two different temperature conditions. The experimental sorption data obtained in the present work were further employed to calculate the distribution coefficient ( $K_d$ ) of iodide on the modified bentonites as representative chemical thermodynamic data.

## 2. Experimental Section

### 2.1. Chemicals for the Iodine–Starch Quantification Method

All experiments were conducted under aerobic conditions. The calibration standard of the aqueous iodide was prepared through the dissolution of iodide standard solution (Sigma-Aldrich, SKU 41271, St. Louis, MO, USA). The concentration of aqueous iodide was set in a range, from 0.04 mM to 0.12 mM, by adding deionized water taken from the water purification system (Merck Millipore, Direct Q5, Burlington, MA, USA). The starch concentration in the aqueous iodide sample was maintained at 0.1%. A starch solution of 1% was prepared through the dissolution of starch (Sigma-Aldrich, SKU S9765) in the deionized water, tempered at  $T = 83 \pm 2$  °C. The acid concentration in the aqueous solution was controlled in a range, from 10 mM to 500 mM, using stock solution of 1 M  $H_2SO_4$  (Merck, SKU 1.09981, Darmstadt, Germany). The concentration of the oxidizing agent was set to 10 mM with either hydrogen peroxide (Sigma-Aldrich, SKU 95321) or potassium

persulfate (Sigma-Aldrich, SKU 216224). The iodine–starch samples were prepared on the day of use, and all chemicals used in the present work were analytical grade.

## 2.2. Modification of Bentonite

The bentonite (Sigma-Aldrich, SKU 285234) was used as the base material for the modification process in this study. The cation exchange capacity (CEC) was found to be  $110 \text{ cmol} \cdot \text{kg}^{-1}$  according to the previous work [11], investigated with the same bentonite used in the present work. The authors of this work note that the experimental method of this study is based on the assumption that the CEC of the bentonite employed in this study is the same as that reported in the literature [11]. For the modification of bentonite, 2 g of bentonite was gently mixed with 100 mL of either 22 mM or 44 mM HDPyCl·H<sub>2</sub>O (Sigma-Aldrich, SKU C9002) solution, equivalent to 100% or 200% CEC of bentonite, respectively, for 24 h at room temperature. After the stirring, the solid samples were centrifuged (4000 rpm, DAIHAN, Cef-D50.6) to discard the supernatant. Subsequently, the bentonite samples were washed with deionized water four times and dried in the vacuum oven (Jeio Tech, OFC-10, Daejeon, Korea) at  $T = 60 \pm 2 \text{ }^\circ\text{C}$  for 24 h. Finally, the HDPy-modified bentonite samples prepared for the adsorption experiments were labeled to be x-Ben, where x indicates the value of the relative concentration of the initial HDPyCl·H<sub>2</sub>O, divided by the CEC of bentonite.

## 2.3. Batch Adsorption Experiments

The iodide adsorption experiments were performed with HDPy-modified bentonite, based on the batch approach. An appropriate amount of modified bentonite (as adsorbent) was dispersed in 1 mM NaI (Sigma-Aldrich, SKU 746371) solution. The liquid-to-solid ratio (L/S ratio) between NaI solution (as adsorbate) and modified bentonite was controlled in a range from 0.1 g/L to 50 g/L. The bentonite suspensions were gently mixed with a rolling mixer (40 rpm, DAIHAN, MixR-40, Seoul, Korea) for 48 h at room temperature to attain the equilibrium condition. For the adsorption experiment at elevated temperature conditions, the bentonite suspensions were tempered at  $T = 50 \pm 5 \text{ }^\circ\text{C}$  and mixed with a magnetic stirring bar (900 rpm) for 48 h. During the equilibrium reaction, an aliquot of bentonite suspensions was taken out as a function of reaction time and ultra-filtered with a membrane filter (10 kDa, Millipore, Burlington, MA, USA) for the quantification of aqueous iodide ions by means of the iodine–starch method.

The adsorption ratio, or removal efficiency, along with the distribution coefficient ( $K_d$ ) of aqueous iodide onto modified bentonite, were calculated according to Equations (1) and (2) [1]:

$$\text{Removal efficiency} = \frac{(C_0 - C_{eq})}{C_0} \quad (1)$$

$$K_d = \frac{(C_0 - C_{eq})}{C_{eq}} \cdot \frac{V}{m} \quad (2)$$

where  $C_0$  represents the initial iodide concentration in the samples,  $C_{eq}$  indicates the iodide concentration after attaining the equilibrium condition,  $V$  is the volume of the solution in  $\text{m}^3$ , and  $m$  represents the mass of the adsorbent in kg. The averaged  $K_d$  values were obtained from the  $K_d$  values, determined at various L/S ratios. However, the samples providing almost complete removal of aqueous iodide were not employed to calculate the averaged values, since the  $K_d$  values could not be reliably quantified under those conditions.

## 2.4. Instruments

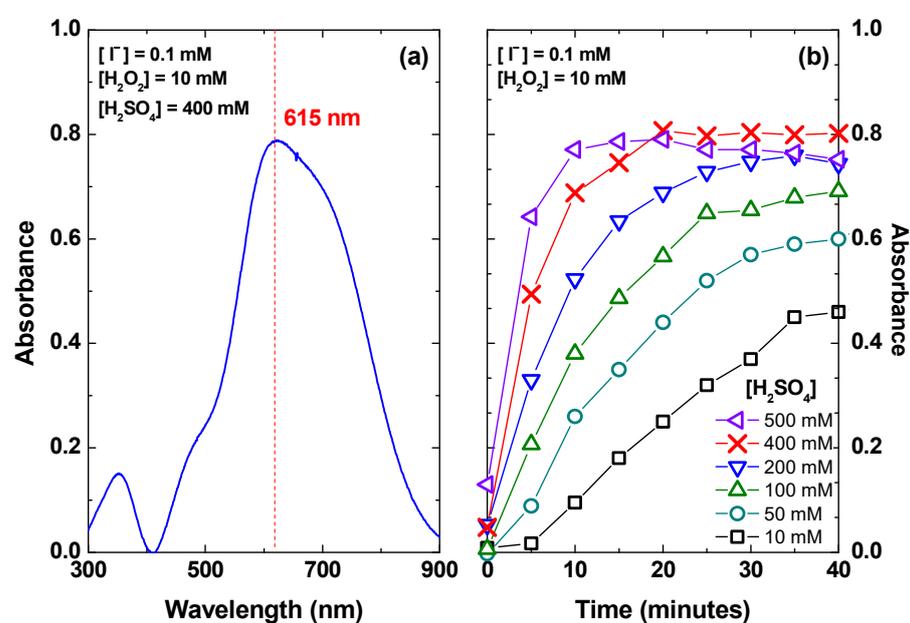
The UV/Vis absorption spectroscopy coupled with the iodine–starch method was employed for the quantification analysis of iodide. The aqueous sample of iodine–starch was transferred to the fused-silica cuvette (Hellma, 111–10-40, 1 cm, Jena, Germany) and analyzed using a photodiode array type UV/Vis spectrophotometer (Analytik Jena, SPECORD S 600, Jena, Germany). The data acquisition and absorption spectrum signal evaluation

were conducted with the WinASPECT PLUS (Analytik Jena, Jena, Germany) and OriginPro 2020 (OriginLab) software programs.

### 3. Results

#### 3.1. Optimization of Iodine–Starch Method

Since the stability of the iodine–starch complex is known to be sensitive to various reaction parameters [10] (e.g., reaction time, types of acids and oxidants, etc.), a systematic investigation was performed to determine the optimized conditions for the iodine–starch method. Figure 1a represents the UV/Vis absorption spectrum of an iodine–starch sample prepared with the standard solution of iodide with known concentration along with 10 mM H<sub>2</sub>O<sub>2</sub> and 400 mM H<sub>2</sub>SO<sub>4</sub>. A relatively broad absorption spectrum, with the absorption peak located at 615 nm, unambiguously indicated the formation of the iodine–starch complex [9,10]. Therefore, the UV/Vis absorbance value determined at 615 nm was selected to be used for further investigation. The authors note that the iodine–starch sample, synthesized with the iodide solution, mixed with un-modified bentonite, and ultra-filtered, showed almost the same UV/Vis absorption spectrum as that prepared with a pure iodide solution.



**Figure 1.** (a) UV/Vis absorption spectrum of iodine–starch complex; and (b) the absorbance at 615 nm, measured as a function of reaction time at various H<sub>2</sub>SO<sub>4</sub> concentrations.

As represented in Figure 1b, a gradual increase in absorbance at 615 nm was identified as a function of reaction time, together with a tendency to converge to a specific absorbance value, depending on the H<sub>2</sub>SO<sub>4</sub> concentration. Relatively low absorbance values and slow reaction rates were measured for diluted H<sub>2</sub>SO<sub>4</sub> concentrations, seemingly due to the inhibition of the formation of iodine and triiodide ion [12], based on Equations (3) and (4):

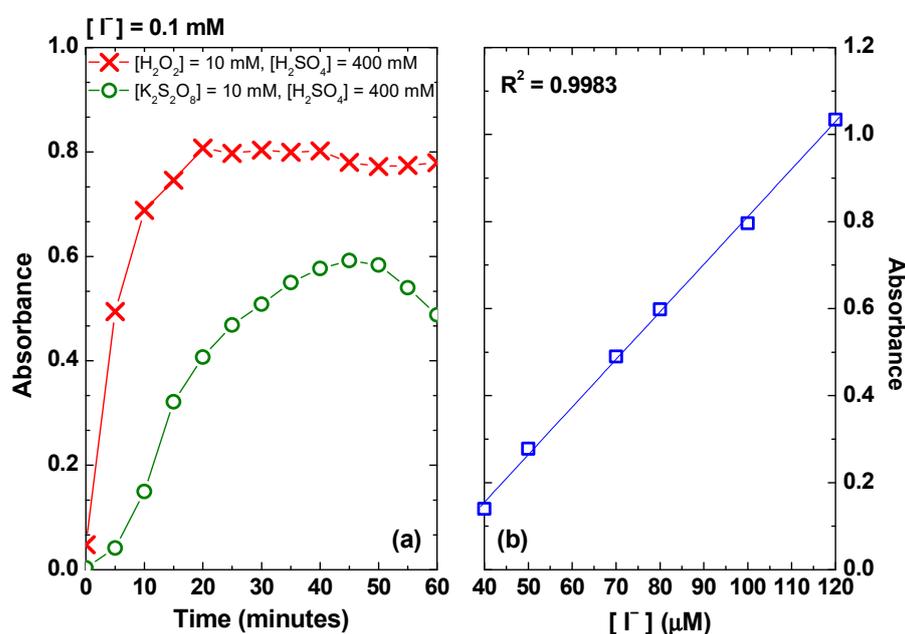
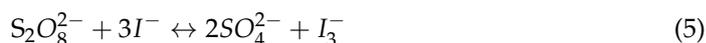


At relatively low H<sub>2</sub>SO<sub>4</sub> concentrations, the chemical reaction described in Equation (3) is predicted to be retarded because of the insufficient H<sup>+</sup> ion. Consequently, the reaction in Equation (4) would also be sequentially hindered, owing to a decreased supply of iodine (I<sub>2</sub>), which is the product of the chemical reaction described in Equation (3).

On the other hand, relatively poor absorbance stability was observed at the highest H<sub>2</sub>SO<sub>4</sub> concentration of 500 mM. The tendency for decreasing absorbance of the iodine–starch complex after ca. 20 min of reaction time at excessively high acidic concentrations,

is relatively consistent with the literature data [13], revealing the gradual enhancement of the acid hydrolysis of starch under the strongly acidic environment. According to the results obtained in the present work, the absorption spectrum of the iodine–starch complex, prepared with 400 mM  $\text{H}_2\text{SO}_4$ , showed a maximum absorbance value ca. 20 min after the sample preparation, with excellent stability over a reaction time of ca. 40 min. Thus, the absorbance values observed at 25, 30, and 35 min were averaged and selectively employed for further investigation (i.e., quantification of aqueous iodide).

In addition, Figure 2a shows the absorbance of the iodine–starch complex at 615 nm, prepared with two different oxidizing agents— $\text{H}_2\text{O}_2$  and  $\text{K}_2\text{S}_2\text{O}_8$ . According to the results, a considerably retarded reaction rate, and a decreased maximum absorbance value, were identified for the sample prepared with 10 mM  $\text{K}_2\text{S}_2\text{O}_8$  as an oxidizing agent, compared with  $\text{H}_2\text{O}_2$ . The reaction between persulfate ions and iodide ions [14] can be described with Equation (5):



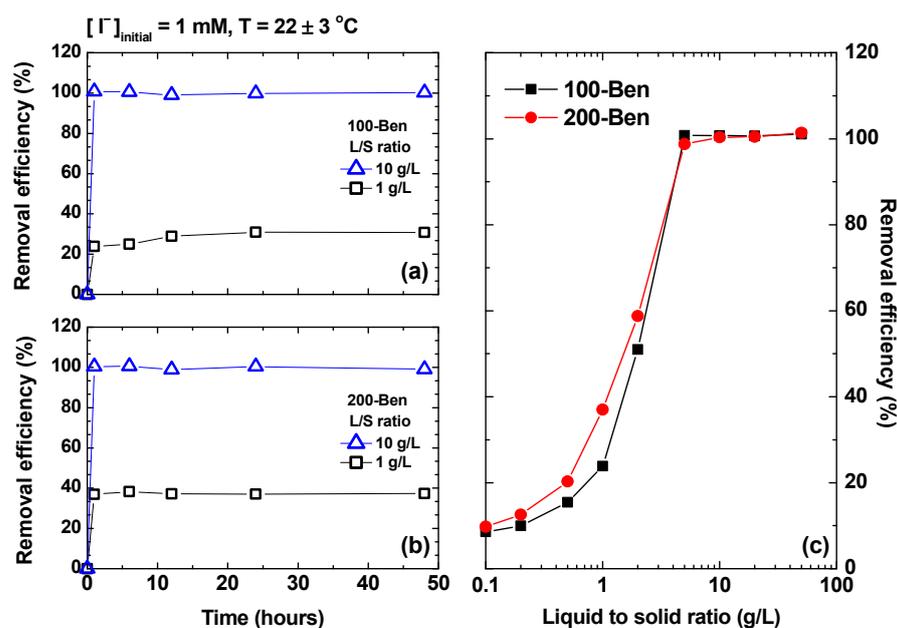
**Figure 2.** (a) UV/Vis absorbance of iodine–starch at 615 nm, prepared by using two different oxidizing agents; (b) the calibration curve of iodine–starch complex, synthesized under the optimized condition (i.e.,  $[\text{H}_2\text{O}_2] = 10 \text{ mM}$ ;  $[\text{H}_2\text{SO}_4] = 400 \text{ mM}$ ; reaction time = 25–35 min).

Thus, the reaction rate of the above chemical equilibrium reaction can apparently be delayed and suppressed due to the excessive amount of sulfate ions provided by the background  $\text{H}_2\text{SO}_4$  solution employed during the sample preparation. The authors also note that the remarkably retarded reaction rate with  $\text{K}_2\text{S}_2\text{O}_8$  could be attributed to the relatively slow oxidation reaction by  $\text{K}_2\text{S}_2\text{O}_8$  compared to  $\text{H}_2\text{O}_2$ , regardless of sulfate ions. Based on the various UV/Vis absorbance results obtained in the present work, the optimized conditions for the quantification of iodide using the iodine–starch method is determined to be  $[\text{H}_2\text{O}_2] = 10 \text{ mM}$  as oxidant;  $[\text{H}_2\text{SO}_4] = 400 \text{ mM}$  as acid; reaction time = 25–35 min.

As shown in Figure 2b, the calibration curve of the iodine–starch complex (obtained with the optimized condition) presents a proportional relationship between the aqueous iodide concentration and the absorbance value. The calibration curve clearly indicates that the iodine–starch method can be further employed for analyzing the sorption behavior of iodide, by quantifying the aqueous iodide ion concentration that remain after the sorption reaction with the HDPy-modified organo-bentonite.

### 3.2. Sorption of Iodide Ion onto the HDPy-Modified Bentonite

As described in the previous section, the iodine–starch method was employed for analyzing the sorption characteristics of iodide ions onto the HDPy-modified bentonite. Figure 3a,b present the removal efficiencies of two different HDPy-modified bentonites (i.e., 100-Ben and 200 Ben) measured at various reaction times. Remarkably rapid sorption reactions, reaching the chemical equilibria within almost 1 h of reaction time, were observed for both modified bentonites at two different liquid-to-solid ratios, indicating the significant sorption affinity of iodide on the HDPy-modified organo-bentonite. The attractive interaction between the iodide ion and the pyridinium ring of the HDPy<sup>+</sup> functional group might be a major driving force for adsorption reactions [4,15]. At the liquid-to-solid ratio of 1 g/L, relatively increased removal efficiency was identified for the 200-Ben sample, in comparison to the 100-Ben sample, which agrees well with literature data [7]. During the modification process, the organic cation (i.e., HDPy<sup>+</sup>) occupies the negatively charged sites on the bentonite surface or interlamination, thus inducing a change of surface charge in the bentonite. Moreover, increased loading of HDPy during the modification process is also expected to induce an increase in the interlayer distance of the bentonite, presumably enhancing the accessibility of HDPy-functionalized interlamination in the modified bentonite [7]. Further detailed structural information for HDPy-modified bentonite can be obtained from the previously reported works [7,15].

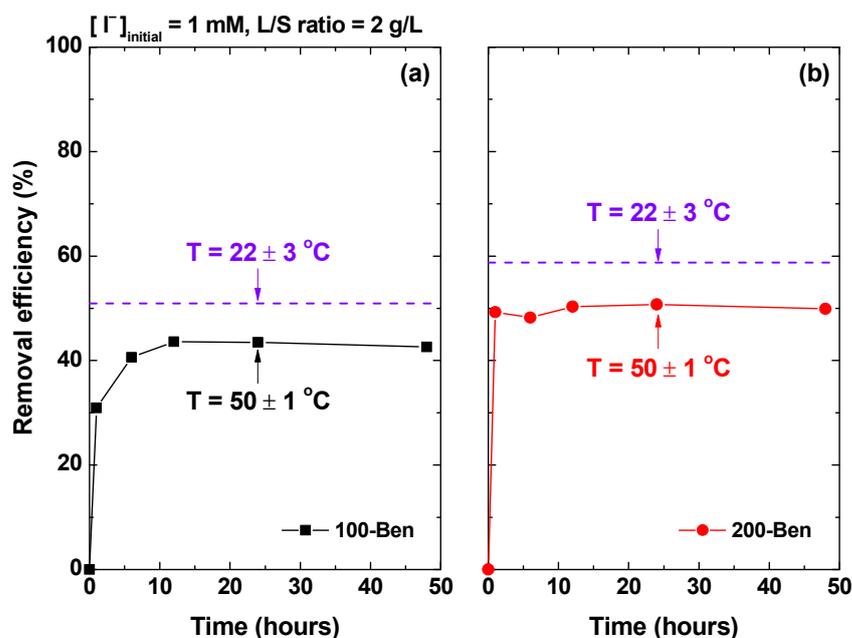


**Figure 3.** Iodide removal efficiency, determined at room temperature as a function of reaction time, for two different HDPy-modified bentonites, such as (a) 100-Ben and (b) 200-Ben; (c) iodide removal efficiencies obtained at various liquid-to-solid ratios, determined at reaction time of 24 h at room temperature. Initial aqueous iodide concentration was set to be 1 mM for all samples.

Furthermore, considerable discrepancies in removal efficiencies between 100-Ben and 200-Ben samples were obtained for all samples determined at liquid-to-solid ratios of lower than 2 g/L, as shown in Figure 3c. On the other hand, almost complete removal of the iodide ions was observed for all bentonite samples equilibrated at liquid-to-solid ratios of higher than 5 g/L. The removal efficiencies determined for the HDPy-modified bentonites with reaction times of 24 h, were selectively employed to calculate the distribution coefficients ( $K_d$ ) of iodide, with the exception of the samples presenting complete removal (i.e., those with the L/S ratio from 5 g/L to 50 g/L).

Moreover, Figure 4 presents the removal efficiencies of HDPy-modified bentonites measured at elevated temperature conditions. In comparison to the analogous experiment

conducted at room temperature, a relatively reduced iodide sorption affinity was identified, to a certain extent, for both modified bentonites at  $T = 50 \pm 5 \text{ }^\circ\text{C}$ , consistent with previously reported data [6]. Although a slight decrease in sorption affinity was observed, the overall rate of sorption reaction was still relatively rapid, even in elevated temperature conditions. The 200-Ben sample reached the chemical equilibrium within 1 h of reaction time, whereas the 100-Ben sample presented a rapid, but slightly decreased, reaction rate, compared with the rate measured at room temperature.

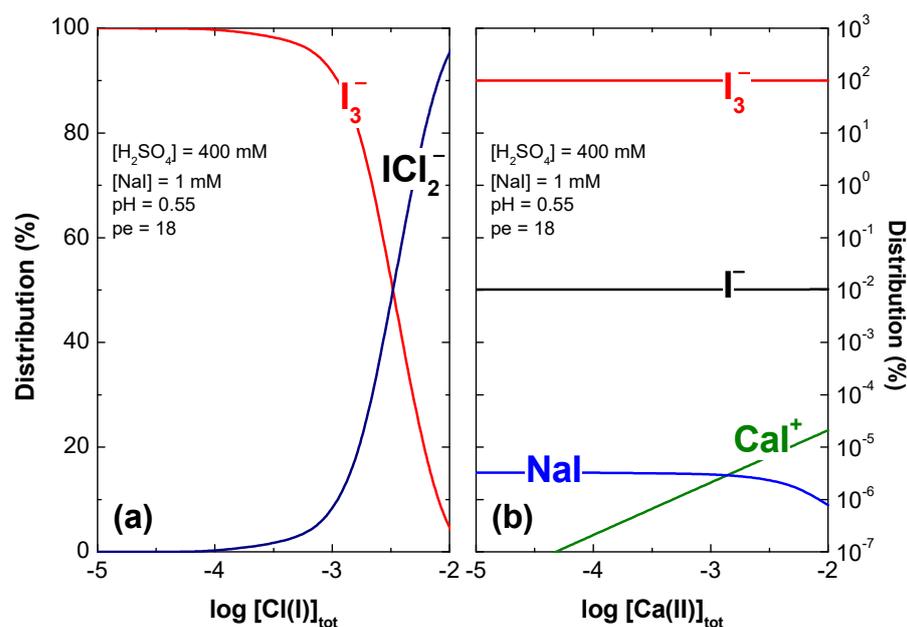


**Figure 4.** Removal efficiencies of (a) 100-Ben and (b) 200-Ben for iodide determined at  $T = 50 \text{ }^\circ\text{C}$ . Dashed line indicates efficiencies obtained at room temperature for comparison.

#### 4. Discussion

According to the experimental results, the iodine–starch method, based on UV/Vis absorption spectroscopy, can be expected to be further utilized for relevant aqueous iodide research. Nonetheless, attention should be paid to factors that could interfere with using the iodine–starch method for reliable quantification analysis. In particular, the formation of triiodide ions ( $\text{I}_3^-$ ), necessary for iodine–starch complexation, is possibly hindered by various cations and anions contained in natural samples. In this regard, the hindrances in the formation of triiodide ions can be evaluated for  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  ions—some of the typical cations and anions in natural groundwater—by using chemical thermodynamic calculations with the PHREEQC computational code [16] and the Andra ThermoChimie database [17]. In the present work, the target system was set to be the aqueous sample for the iodine–starch method (i.e.,  $[\text{H}_2\text{SO}_4] = 400 \text{ mM}$ ,  $[\text{NaI}] = 1 \text{ mM}$ ) under strongly acidic and oxidizing conditions. Note that the pH was fixed to be 0.55 to achieve the convergence in the calculation.

As presented in Figure 5a, a remarkable decrease in the relative portion of triiodide ions in the aqueous sample was predicted at  $[\text{Cl(I)}]_{\text{tot}} > \text{ca. } 1 \text{ mM}$ , due to the significant formation of  $\text{ICl}_2^-$  complex. Therefore, some uncertainty in the quantification of iodide by using the iodine–starch method can probably be expected at the millimolar level of chloride ions. However, Figure 5b indicates that the influence of  $\text{Ca}^{2+}$  ions on the formation of triiodide ions is almost negligible, even at  $[\text{Ca(II)}]_{\text{tot}} = 10 \text{ mM}$ , because of the weak complexation affinity of  $\text{Ca}^{2+}$  with iodide ions. The other major cations in the natural groundwater system, such as  $\text{Na}^+$  and  $\text{Mg}^{2+}$  ions, also provide similar tendencies to  $\text{Ca}^{2+}$  ion.



**Figure 5.** Species distribution of iodine for various (a)  $\text{Cl}^-$  and (b)  $\text{Ca}^{2+}$  concentrations. Note that the  $y$ -axis of the left-hand side figure is in linear scale, and that of the right-hand side figure is in log scale.

Thus, the chemical thermodynamic calculation revealed that the matrix effects, particularly of the anions in natural groundwater, require further clarification to be reliable when using the iodine–starch method in the quantification of iodide in natural samples. The authors note that the absence of chloride ions in the aqueous solution equilibrated with HDPy-modified bentonites in the present work was confirmed using the  $\text{AgCl}$  precipitation method [18] with 1 M  $\text{AgNO}_3$  solution.

Table 1 presents the distribution of iodide coefficients obtained in the present work for the samples with L/S ratios from 0.1 g/L to 2 g/L, along with those taken from the literature [4,6]. Based on the considerable uncertainty that can usually be expected in various adsorption studies [19,20], averaged  $K_d$  values of  $0.54 \pm 0.25 \text{ m}^3 \cdot \text{kg}^{-1}$  and  $0.72 \pm 0.22 \text{ m}^3 \cdot \text{kg}^{-1}$  for HDPy<sup>+</sup> loadings of 100% and 200% CEC of bentonite at room temperature, respectively, were assessed to be relatively comparable to literature data. The tendency of the  $K_d$  values to increase with a decrease in L/S ratios also shows relative consistency with literature data [21]. Furthermore, the  $K_d$  values of the samples equilibrated at elevated temperature conditions were determined to be  $0.39 \pm 0.25 \text{ m}^3 \cdot \text{kg}^{-1}$  and  $0.51 \pm 0.25 \text{ m}^3 \cdot \text{kg}^{-1}$  for 100-Ben and 200-Ben samples, respectively. The authors note that, due to the relatively low removal capacity compared to those determined at room temperature, the uncertainty associated with  $K_d$  values obtained at  $T = 50 \pm 5 \text{ }^\circ\text{C}$  was set to  $\pm 0.25$ , based on the uncertainty of  $K_d$  values calculated at room temperature.

The slight discrepancies among the various available  $K_d$  values might be caused by different structural characteristics of the base materials employed, i.e., bentonite (present work, Sigma-Aldrich, SKU 285234), natural bentonite (Rajasthan, India) [4], and MX-80 (Wyoming, USA) [6]. The relatively large interlayer distance of the bentonite employed in the present work ( $d = 15.2 \text{ \AA}$  [22]), compared to natural bentonite ( $d = 12.8 \text{ \AA}$  [4]) and MX-80 ( $d = 9.5 \text{ \AA}$  [23]), might enhance the access of iodide to the HDPy<sup>+</sup> functional group, providing a hint toward higher  $K_d$  values.

**Table 1.** The distribution coefficients of iodide obtained for HDPy-modified organo-bentonites at various conditions.

Mineral	T (°C)	HDPy-CEC <sup>1</sup>	L/S Ratio (g/L)	Working Solution	K <sub>d</sub> (m <sup>3</sup> ·kg <sup>-1</sup> )	Ref.	
Bentonite	RT	100%	0.1	[I <sup>-</sup> ] = 1.0 mM	0.94	p.w.	
			0.2		0.55		
			0.5		0.36		
			1		0.31		
			2		0.52		
			Avg.		0.54 ± 0.25		
			0.1		1.08		
	200%	0.2	0.72				
		0.5	0.51				
		1	0.59				
		2	0.71				
		Avg.	0.72 ± 0.22				
		50 ± 5	100%		2		0.39 ± 0.25 <sup>2</sup>
			200%		2		0.51 ± 0.25 <sup>2</sup>
Natural Bentonite	RT	100%	10	[I <sup>-</sup> ] = 0.78–7.88 mM	0.184	[4]	
MX-80	20	200%	50	[I <sup>-</sup> ] = 10 <sup>-9</sup> –10 <sup>-2</sup> M; SGW <sup>3</sup>	0.297	[6]	
	50	200%	50		0.162	[6]	

<sup>1</sup> HDPy loading equivalent to cation exchange capacity (CEC) of the mineral; <sup>2</sup> the uncertainty was re-assessed by the authors; <sup>3</sup> synthetic groundwater [6] with ionic strength ≈ 0.037 M.

## 5. Conclusions

UV/Vis absorption spectroscopy coupled with the iodine–starch method was employed to investigate the sorption behavior of iodide on modified organo-bentonites. A relatively broad, but clear absorption peak, located at 615 nm, indicated the formation of the iodine–starch complex. The optimized condition for the quantification of iodide was determined according to the absorbance values observed with various experimental conditions, such as reaction time, acid concentration, and oxidizing agent. Based on the proportional relationship between the iodide concentration and absorbance value, the iodine–starch method was further employed to analyze the sorption characteristics of iodide onto the HDPy-modified bentonites.

Two different types of modified bentonites, i.e., 100-Ben and 200-Ben, showed significantly fast sorption reaction rates and remarkable sorption affinities for iodide ions in the aqueous solution. The adsorptive reaction between the iodide ion and the modified bentonite was mainly due to the pyridinium ring of the HDPy<sup>+</sup> functional group on the surface or interlamination of bentonite. The K<sub>d</sub> values of 100-Ben and 200-Ben (determined at room temperature; T = 50 ± 5 °C) were relatively comparable with previously reported literature data. The minor discrepancies among the various K<sub>d</sub> values of modified bentonites might be attributed to the structural characteristics of the base materials, such as interlayer distances, which are correlated with the access of iodide ions to the HDPy<sup>+</sup> functional group.

To the best of the authors' knowledge, this work is the first application of the iodine–starch method coupled with UV/Vis absorption spectroscopy to analyze the sorption affinity of iodide on organo-clay minerals. According to the results, this work clearly confirmed that the iodine–starch method can be employed in the iodide sorption experiments. As a rapid, simple, and inexpensive method for the iodide quantification, the UV/Vis absorption spectroscopy, based on the iodide–starch method, is expected to be further

utilized for relevant aqueous iodide research in the future. Nevertheless, the authors note that in order to apply the iodine–starch method to the natural environment samples, further experimental efforts are required to confirm the presumable influences of the sample matrix on the quantification analysis results.

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