Spectrophotometric Study on Kinetics and Thermodynamics of Adsorption and Catalytic Transformation of K₂Cr₂O₇ to K₂CrO₄ by Natural Hermit Crab Shell Powder

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Abstract

The adsorption and transformation of $K_2Cr_2O_7$ at natural hermit crab shell powder was studied by UV-visible spectrophotometry. $K_2Cr_2O_7$ is adsorbed at natural hermit crab shell powder, and follows the Freundlich adsorption model with the adsorption constant of K_F =888.8 and adsorption free energy change of 16.83 kJ.mol⁻¹. The adsorbed $K_2Cr_2O_7$ is catalytically transformed into K_2CrO_4 in moderate conditions by natural hermit crab shell powder with the apparent first-order rate constant of 0.0219 s⁻¹, and equilibrium constant of K=2.27×10¹² M⁻¹.

Keywords: Natural hermit crab shell powder; K₂Cr₂O₇; catalysis; kinetics; thermodynamics; UV-visible spectrophotometry.

1. Introduction

Compared to Cr(III), Cr(VI) is a more harmful toxic species to the human normal nervous system, immune system, internal secretion system and a cause of cancers [1], and cannot be directly decomposed by microbes in environment [2]. The removal of Cr (VI) from environment had been reported with chemical or physical adsorptions [3], or bioadsorption [4-8]. The transformation of Cr (VI) to Cr(III) may be used to reduce the toxicity of Cr (VI). Among Cr (VI) compounds, the toxicity of K₂Cr₂O₇ is stronger than K₂CrO₄ [9]. The transformation from K₂Cr₂O₇ to K₂CrO₄ is commonly catalyzed by strong bases [10]. In acidic solution, Cr (VI) is mainly in K₂Cr₂O₇ form, but in weak base or base solution, the main form of Cr (VI) is K₂CrO₄.

The natural hermit crab shell is an important natural polymer mainly composed of calcium carbonate, chitin and chitosan with the twisted lamellar structure in the endocuticle and the ribbon shape pore canal tubule in the exocuticle [11]. The strong bioadsorption of natural hermit crab shell for Cr (VI) has been studied with a well adsorption model [12]. In our previous work on the electrochemical determination of Cr (VI) experiments with natural hermit crab shell powder modified electrode [13], it was found that the natural hermit crab shell powder not only adsorbs Cr (VI) effectively but also shows a catalytic transformation from $K_2Cr_2O_7$ to K_2CrO_4 . In the present paper, the adsorption and catalytic behavior of natural hermit crab shell to Cr (VI) were studied by UV-visible spectrophotometry [14], and some interesting results are reported here.

2. Methods

2.1. Instruments and materials

The spectrophotometric experiments were carried out on UV-visible spectrophotometer (UV-Lamda 25, Perkin-Elmer Co., USA). The hermit crab shell powder was separated from the system by centrifugal separation with CT6T centrifugal machine (Tianmei Biochemical Device Instrument Engineering Co., Shanghai, China). Crab shells were collected from hairy crabs purchased from Suxiege Co., Shanghai, and cleaned with drinking water and ultrapure water. Potassium dichromate ($K_2Cr_2O_7$), potassium chromate (K_2CrO_4), disodium hydrogen phosphate (Na_2HPO_4), citric acid and hydrochloric acid (HCI) were all analytical pure (purchased from Shenyang Chemical Co.), and all solutions were prepared with ultrapure water (18.2 M Ω cm⁻¹) prepared with Milli-Q system (Billerica, MA, USA).

2.2. Experimental procedure

Dried clean natural hermit crab shell was grounded into powder (about 80-100#) with grinder. The natural hermit crab powder 0.0500g was mixed with $5mL \ 1.0 \times 10^{-4}M$ potassium dichromate solution in 10mL centrifugal tube for adsorption. After adsorption for certain time, the mixture was centrifuged at 4500 rpm (at 25°C for 5 min). The obtained supernatant solution was taken for UV-visible spectrophotometric experiments.

3. Results and Discussion

3.1. UV-visible spectrophotometry of Cr(VI)

The UV-visible spectra of Cr(VI) solutions before and after the adsorption and catalysis with hermit crab shell powder were shown in Figure 1. K_2CrO_4 solution shows a UV-visible spectrum with absorption peaks at 273nm and 370nm (curve 2 in Figure 1). $K_2Cr_2O_7$ solution gives out a spectrum with absorption peaks at 257nm and 350nm (curve 3 in Figure 1). After treatment with hermit crab shell powder, $K_2Cr_2O_7$ solution shows an identical spectrum of K_2CrO_4 with absorption peaks at 273nm and 370nm (curve 4 in Figure 1). These results indicate that the $K_2Cr_2O_7$ is catalyzed by hermit crab shell powder, and transforms into K_2CrO_4 during the treatment. According to the literature [10], the transformation reaction is described as,

$$Cr_2O_7^{2-}+2OH^{-}=2CrO_4^{2-}+H_2O$$
 (1)

So, the absorbance of the peak in curve 4 is about 2 times higher than that in curve 2.

Natural hermit crab shell is a lamellar structural material with ribbon shape pore canal tubule in the exocuticle [11]. The canal tubule with elliptical shaped cavities is about 15-25 μ m in diameter [15]. The cavity is full of -NH⁺₂, -CO, and -CH₃ groups, which absorbs Cr₂O₇²⁻ [16] and transforms Cr₂O₇²⁻ into CrO₄²⁻. As we know, the natural hermit crab shell has been used to absorb Cr (VI) [12]. But the hermit crab shell powder with this kind catalysis behavior has not been found and studied. This catalytic behavior may be a useful property of natural materials beyond the chemical adsorption, which open a new way to explore the natural hermit crab shell and other natural materials with the inside structures with high selectivity and catalytic activity [17-20].

(4)

3.2. Thermodynamics of transformation reaction

According to the reaction (1), the reaction equilibrium constant can be expressed as,

$$\mathbf{K} = \frac{\left[\mathbf{Cr}\mathbf{O}_{4}^{2^{-}}\right]^{2}}{\left[\mathbf{Cr}_{2}\mathbf{O}_{7}^{2^{-}}\right]\left[\mathbf{OH}^{-}\right]^{2}}$$
(2)

Here, [species] indicates the equilibrium value of the species. The distribution of species of CrO_4^{2-} in the system can be expressed as,

$$\delta_{\text{CrO}_{4}^{2^{-}}} = \frac{\frac{1}{2} \text{K} \left[\text{OH}^{-} \right]^{2}}{\frac{1}{2} \text{K} \left[\text{OH}^{-} \right]^{2} + \left[\text{CrO}_{4}^{2^{-}} \right]}$$
(3)

The reaction equilibrium constant can be obtained from the following equation,

$$K = \frac{2\left[CrO_{4}^{2^{-}}\right]}{\left[OH^{-}\right]^{2}}, \text{if } \delta_{CrO_{4}^{2^{-}}} = 0.5$$

The transformation between $Cr_2O_7^{2^-}$ and $CrO_4^{2^-}$ can also been realized by changing the pH in medium [10]. So, the reaction equilibrium constant can be obtained by spectrophotometry with different solution pH. The solution pH was controlled by disodium hydrogen phosphate-citric acid buffer system in the range of 2.2~8.0. UV-visible spectrophotometric experiment were performed in the buffer solution including 1.0×10^4 M K₂Cr₂O₇, the obtained spectra were shown in Figure 2a. The absorbance at 370 nm obtained from the spectra with

different solution pH was normalized by equation of $A_n = \frac{A - A_{2,2}}{A_{8,0} - A_{2,2}}$, where A_n was the normalized

absorbance, $A_{2.2}$ was the absorbance at pH 2.2, and $A_{8.0}$ was the absorbance at pH 8.0. The normalized absorbance was plotted against solution pH as shown in Figure 2b. The curve was regressed with Boltzmann model with an equation of

$$A_{n} = 0.9936 - \frac{0.9789}{\left(1 + \exp\left[\left(pH - 5.973\right)/0.402\right]\right)}, R^{2} = 0.997$$
(5)

From this equation, it was obtained that the middle point of the curve located at $\delta_{CrO_4^{2-}} = 0.5$, and pH=5.973,

so the reaction equilibrium constant can be estimated as $K=2.27\times10^{12}$ M⁻¹. The larger value of the equilibrium constant indicates the process is thermodynamically favorable one, and can kinetically be driven by catalysts such as OH⁻ and other base groups.

3.3. Catalytic kinetics of Cr(VI) by hermit crab shell powder

The transformation kinetics of $Cr_2O_7^{2-}$ into CrO_4^{2-} catalyzed by natural hermit crab shell powder was monitored by UV-visible spectrophotometry. The natural hermit crab shell power of 0.0300g was added into 3mL

 1.0×10^{-4} M K₂Cr₂O₇ in a cuvette in the chamber of spectroscopy, then the spectroscopic experiments were carried out successively. The obtained ultraviolet spectra were as shown in Figure 3a. The plot of absorbance at 370nm against time was a sigmoidal curve as shown in Figure 3b. The kinetic curve was regressed as a Boltzmann model [21] with an equation of

A =
$$1.66 \cdot 1.66 \times \exp(-0.00204 \times t/\min)$$

R²=0.994, SD=0.0199 (6)

The apparent first-order reaction rate constant can be obtained as 0.00204 min⁻¹.

The total process of adsorption and transformation can be evaluated by the adsorption isothermal equation with different concentration of $K_2Cr_2O_7$. The natural hermit crab shell power of 0.0500g was added into 5mL $K_2Cr_2O_7$ in the concentration range of 5. 0×10^{-6} — 5.0×10^{-4} M in 10mL centrifugal tube, and centrifugalized for 5 min. After centrifugation, the supernatant was transferred into a cuvette for spectroscopic experiments. The absorbance at 370 nm of the obtained ultraviolet spectra was plotted against concentration of $K_2Cr_2O_7$ shown in Figure 4a. The regression equation follows an exponential dissociation function

$$A = 2.587 - 2.587 \times \exp(-5426 \times c/M)$$

$$R^{2} = 0.998, SD = 0.0504$$
(7)

According to Freundlich adsorption model [22, 23], plot of log(A) against log(c) is a straight line as shown in Figure 4b with a regression equation of

$$log(A) = 2.949 + 0.747log(c / M),$$

$$R^{2}=0.984, SD=0.084$$
(8)

From the equation (8), the adsorption constant of $K_F=888.8$ and n=1.34 were obtained. The adsorption free energy change [24] was calculated as 16.83 kJmol⁻¹. These results indicate that the adsorption of $Cr_2O_7^{2-}$ ion in the cavity of the natural hermit crab shell power is favorable process, and $Cr_2O_7^{2-}$ ion is transformed into CrO_4^{2-} , and released from the cavity. This transformation reaction between chromates can also be catalyzed by strong acid (pH<3.0) or strong base (pH>10.0), while hermit crab shell powder can catalyze the reaction in moderate pH range (pH: 10-3.0), and may be used in the catalytic transformation of $Cr_2O_7^{2-}$ to CrO_4^{2-} .

4. Conclusion

In the present paper, the adsorption and transformation of $K_2Cr_2O_7$ into K_2CrO_4 with natural hermit crab shell powder in moderate pH was studied by UV-visible spectrophotometry. The adsorption follows a Freundlich adsorption isotherm model with favorable adsorption constant. The transformation kinetics follows a Boltzmann equation. The transformation reaction shows a larger equilibrium constant obtained from relationship between absorbance of K_2CrO_4 at 370nm and solution pH, which offers a suitable method for the transformation from $K_2Cr_2O_7$ to K_2CrO_4 in moderate conditions. The catalytic activity may be due to the inside structure of natural hermit crab shell powder.

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Competing Interests

Authors declare that they have no competing interests.

Authors' Contributions

All authors contributed equally to this work.

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Figure 1: UV-visible spectra of background (1), K_2CrO_4 (2), $K_2Cr_2O_7$ (3) and $K_2Cr_2O_7$ treated with hermit crab shell powder (4). Concentrations of K_2CrO_4 and $K_2Cr_2O_7$ were 1.0×10^{-4} M; solution pH: 5.



Figure 2: The ultraviolet spectra of K₂Cr₂O₇ aqueous solution at different pH (a) and relationship between absorbance at 370 nm and solution pH (b). Solution pH: 1,8.0; 2,6.8; 3,6.0; 4,5.6; 5,5.2; 6,2.2; 7, background. Other experimental conditions were the same as those in Figure 1.

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Figure 3: The ultraviolet spectra of K₂Cr₂O₇ aqueous solution with different catalytic time (a) and the relationship between absorbance at 370nm and catalytic time (b). Catalytic time (t/min): 1,180; 2,160; 3,140; 4,110; 5,80; 6,60; 7,40; 8,30; 9,0; 10, background. Other experimental conditions were the same as those in Figure 1.



Figure 4: The relationships between absorbance of K₂Cr₂O₇ at 370nm and concentration (a) and its double logarithm plot

(b).