



## Mechanism of Cr(VI) adsorption by coir pith studied by ESR and adsorption kinetic

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### ABSTRACT

The oxidation state of chromium in coir pith after Cr(VI) adsorption from aqueous solution was investigated using electron spin resonance (ESR). To elucidate the mechanism of chromium adsorption on coir pith, the adsorption studies of Cr(VI) onto lignin,  $\alpha$ -cellulose and holocellulose extracted from coir pith were also studied. ESR signals of Cr(V) and Cr(III) were observed in coir pith adsorbed Cr(VI) at solution pH 2, while ESR spectra of lignin extracted from coir pith revealed only the Cr(III) signal. In addition, ESR signal of Cr(V) was observed in  $\alpha$ -cellulose and holocellulose extracted from coir pith adsorbed Cr(VI). These results confirmed that lignin in coir pith reduced Cr(VI) to Cr(III) while  $\alpha$ -cellulose and holocellulose extracted from coir pith reduced Cr(VI) to Cr(V). The Cr(V) signal exhibited in ESR of  $\alpha$ -cellulose and holocellulose might be bound with glucose in cellulose part of coir pith. In addition, xylose which is main in pentosan part of coir pith, indicated that it is involved in form complex with Cr(V) on coir pith. The adsorption kinetic of Cr(VI) from aqueous solution on coir pith was also investigated and described well with pseudo second order model. ESR and desorption experiments confirmed that Cr(VI), Cr(V) and Cr(III), exist in coir pith after Cr(VI) adsorption. The desorption data indicated that the percentage of Cr(VI), Cr(V) and Cr(III) in coir pith were 15.63%, 12.89% and 71.48%, respectively.

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### 1. Introduction

Chromium is a widespread contaminant in the environment which originates from the emissions of industry including electroplating, pigment, metal cleaning, leather processing and mining. Chromium exists in natural water in two stable oxidation states, Cr(VI) and Cr(III). Cr(VI) is more toxic, a powerful carcinogenic agent and causes epigastric pain, nausea, vomiting, severe diarrhea and hemorrhaging [1]. Therefore, it is essential to remove chromium contamination from wastewater. Many conventional methods have been investigated to remove chromium such as chemical reduction, ion exchange, precipitation, reverse osmosis and electro dialysis [1–3]. However, these methods are not widely practiced due to their high operational costs and problems in the disposal of the residual metal sludges [4]. In contrast, the adsorption method uses inexpensive adsorbents as an economically feasible alternative for chromium removal due to its efficiency and low operational costs.

Previous research has reported that the reduction of Cr(VI) to Cr(III) occurs after Cr(VI) adsorbs with living plants such as subterranean clover [5], wetland plants [6], bacteria [7,8] and biomass (non-living biological substances) such as hops biomass [9], rice husk [10], dead fugal biomass [11], and oat byproducts [12]. In addition, other literature reports that electron spin resonance (ESR) experiments provide evidence of the reduction of Cr(VI) to Cr(III) through an intermediate Cr(V) species by living plant and bacteria [5–8]. In our previous research, coir pith, a byproduct padding from mattress factories, was used as an adsorbent for Cr(VI) adsorption. This adsorbent was effective and had high capacity for Cr(VI) adsorption [13]. However, the actual chromium oxidation state, uptake and binding to coir pith after Cr(VI) adsorption have not been investigated. ESR is a useful technique for providing information on the oxidation state of the element under investigation.

This study focuses on the oxidation state of chromium in coir pith after Cr(VI) adsorption using electron spin resonance to elucidate the mechanism of chromium adsorption. The lignin, holocellulose and  $\alpha$ -cellulose extracted from coir pith adsorbed Cr(VI) were studied by ESR. The adsorption kinetics of Cr(VI) adsorption on coir pith and desorption were also investigated.

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## 2. Methodology

### 2.1. Adsorbents preparation

Coir pith was obtained as a waste product from padding used in mattress factories, Prachuapkhirikhan province (Thailand). It was dried in ambient air and then crushed and sieved to obtain an approximate particle size less than  $75\ \mu\text{m}$  ( $-200$  mesh, U.S. standard sieve). Lignin, holocellulose and  $\alpha$ -cellulose were extracted from coir pith according to the following standard methods: TAPPI T 222 om-88 for lignin [14], TAPPI T 203 om-93 for  $\alpha$ -cellulose [15] and browning method for holocellulose [16]. In addition, D-glucose and D-xylose were obtained from Merck Ltd., Thailand.

### 2.2. Cr(V) preparation

$\text{Na}[\text{Cr}(\text{O})(\text{ehba})_2]\cdot\text{H}_2\text{O}$  for Cr(V) standard in ESR experiments was synthesized from 2-ethyl-2 hydroxylbutanoic acid and sodium dichromate in acetone [17]. To a solution of 19.8 g of 2-ethyl-2 hydroxylbutanoic acid in 125 ml of acetone in a 300 ml Erlenmeyer flask is added 6.5 g of anhydrous sodium dichromate and the heterogeneous mixture is stirred magnetically until the dichromate is completely dissolved (about 10 min). The flask is fitted with glass stopper and immersed in a temperature controlled water bath at  $25\ ^\circ\text{C}$  for a period of 24 h. The solution is poured into 375 ml of hexane, whereupon the chromium (V) complex precipitates as a dark red-violet solid. The crude product is collected, dried in freeze-dried machine for 30 min to remove water and volatile materials.

### 2.3. Cr(VI) adsorption experiments

Batch experiments were conducted in a 20 ml sealed glass bottle containing 0.2 g of adsorbents and 10 ml of Cr(VI) solution prepared from potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ). The bottle was shaken at 150 rpm in the solution pH of 1, 2 and 10 at  $30\ ^\circ\text{C}$  and contact time of 30 min, 1–6, 18 h. The reaction mixture was filtered through the filter paper. The Cr(VI) concentration remaining in the supernatant was measured using a spectrophotometer (Spectronic 21, BAUSCH & LOMB) through the development of a purple-violet color with 1,5-diphenyl carbazide in an acidic solution at a wavelength of 540 nm. Adsorption kinetics of Cr(VI) on coir pith were also investigated by varying the initial contact time from 5 to 420 min.

### 2.4. Electron spin resonance (ESR) measurements

Ten milligram samples were loaded into a quartz sample tube with 5 mm diameter, and then analyzed by electron spin resonance using X-band ESR spectrometer (JEOL, JES TE-100) under the operation conditions of microwave power 5 mW, a microwave frequency 9.44 GHz, an external magnetic field of 340 mT, a field amplitude 10 mT, a field modulation 100 kHz, a modulation width 0.1 mT, a time constant 0.1 s, and sweep time of 2 min. In addition,  $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$  and  $\text{Na}[\text{Cr}(\text{O})(\text{ehba})_2]\cdot\text{H}_2\text{O}$  were used as Cr(III) and Cr(V) standard, respectively, in ESR experiments.

### 2.5. Desorption study

The desorption study was carried out by agitating 0.2 g of chromium-adsorbed adsorbents with 10 ml of 1 M NaOH and 2 M  $\text{HNO}_3$  at  $30\ ^\circ\text{C}$  and shaken at 150 rpm for 24 h. Then, the sample was filtered by filter paper and the total chromium in the residual solution was determined by Inductively Couple Plasma Spectrometer (ICP), Jobin Yvon-JY 124, France. The Cr(VI) remaining in solution was measured using a spectrophotometer (Spectronic 21, BAUSCH

& LOMB) through the development of a purple-violet color with 1,5-diphenyl carbazide in an acidic solution at a wavelength of 540 nm. The difference in concentration between the total and hexavalent chromium (Cr(VI)) was taken as the concentration of trivalent chromium, Cr(III).

## 3. Results and discussion

### 3.1. Cr(VI) adsorption

Batch experiments were carried out on the adsorption of Cr(VI) by coir pith, lignin extracted from coir pith, holocellulose extracted from coir pith and  $\alpha$ -cellulose extracted from coir pith at an adsorbent dosage of 2% (w/v), solution pH 1, 2 and 10, contact time of 18 h and temperature of  $30\ ^\circ\text{C}$ . The results presented that the percentages of Cr(VI) adsorption on holocellulose extracted from coir pith (23.22% at solution pH 1, 16.92% at solution pH 2, 5.03% at solution pH 10) and  $\alpha$ -cellulose extracted from coir pith (16.14% at solution pH 1, 6.94% at solution pH 2, 0.99% at solution pH 10) at all solution pH were quite low, while the percentages of Cr(VI) adsorption on lignin extracted from coir pith (75.74% at solution pH 1, 84.63% at solution pH 2, 30.49% at solution pH 10) and coir pith itself (65.64% at solution pH 1, 67.62% at solution pH 2, 16.61% at solution pH 10) were high. However, the percentages of Cr(VI) adsorption onto coir pith itself were lower than lignin extracted from coir pith. In addition, the results indicated that the maximum Cr(VI) adsorption percentage on lignin extracted from coir pith was observed at solution pH 2. These results confirmed that lignin extracted from coir pith has excellent ability to adsorb Cr(VI). The coir pith is a potential adsorbent for removal of Cr(VI) due to the fact that coir pith is composed of approximately 36% lignin.

### 3.2. ESR of Cr(VI) adsorption by coir pith at various solution pH

The oxidation state of chromium adsorbed on coir pith after Cr(VI) adsorption was measured by electron spin resonance. ESR is a physical method for observing resonance adsorption of microwave power by unpaired electron spins states in a magnetic field. Cr(III), containing unpaired electrons is ESR positive and Cr(V) is also positive, while Cr(VI) with no unpaired electron is ESR negative. The ESR spectra of coir pith adsorbed Cr(VI) at various solution pH is shown in Fig. 1. As can be seen, the ESR spectra of coir pith adsorbed Cr(VI) at solution pH 2 and pH 10 exhibited the signal with

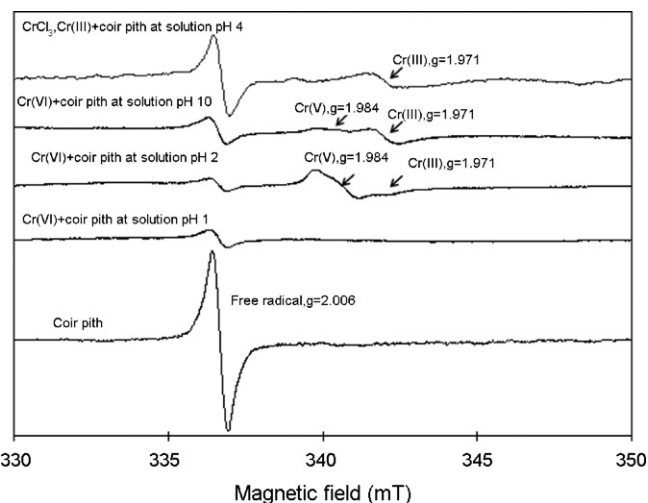
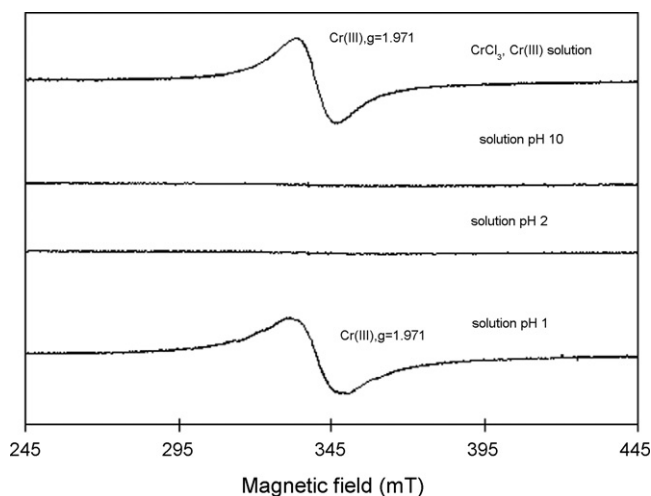


Fig. 1. ESR spectra of coir pith adsorbed Cr(VI) at various solution pH (conditions: Cr(VI) concentration =  $990\ \text{mg l}^{-1}$ , contact time 18 h,  $30\ ^\circ\text{C}$ , dosage = 2% w/v).

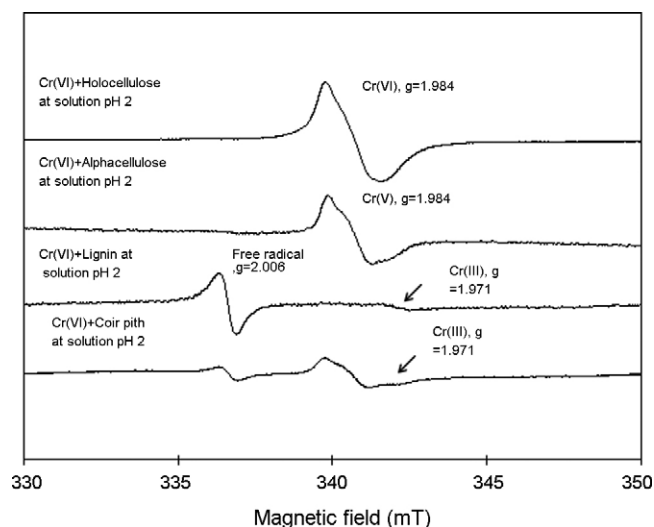


**Fig. 2.** ESR spectra for residual solution from Cr(VI) adsorption by coir pith at various solution pH.

$g = 1.971$  for Cr(III),  $g = 1.984$  for Cr(V) and the large signal of free radical ( $g = 2.006$ ) in coir pith. These results indicated two reducing processes, Cr(VI) to Cr(V) and Cr(VI) to Cr(III) exist. ESR spectra of residual solution in various pH was also shown in Fig. 2. Cr(III) and Cr(V) were not observed in the residual solution in solution pH 2 and 10. This might be confirmed that the reduction process of Cr(VI) to Cr(V) and Cr(VI) to Cr(III) only occurred on coir pith surface after Cr(VI) adsorption. On the other hand, Cr(III) revealed in the residual solution in the solution at pH 1. This explained that Cr(III) in solution at pH 1 occurred from the direct reduction process of Cr(VI) to Cr(III) in solution because of strong acidic solution. The solution had shown color change to green-grey. The Cr(III) in solution was not favorably adsorbed on the coir pith due to the electrostatic repulsion between  $\text{Cr}^{3+}$  and positively charged coir pith. However, the partial of Cr(VI) at solution pH 1 could be adsorbed on the coir pith surface which the electrostatic attraction occurred between the positively charged coir pith and negatively charged  $\text{HCrO}_4^-$ , but the ESR of Cr(III) signal on coir pith surface was not clearly observed (Fig. 1). This due to the fact that the reduction of Cr(VI) to Cr(III) occurred very quite low because the percentage of Cr(VI) adsorption on coir pith is lower in comparison with lignin adsorbed Cr(VI) at solution pH 1 and coir pith at solution pH 2.

Coir pith contains major two components, lignin and cellulose (lignin 36%, holocellulose 43.8%,  $\alpha$ -cellulose 27.8%). Therefore, the ESR analysis of lignin,  $\alpha$ -cellulose and holocellulose extracted from coir pith adsorbed Cr(VI) at solution pH 2 were also investigated to clarify the mechanism of Cr(VI) adsorption on coir pith. (Fig. 3). The Cr(VI) signal ( $g = 1.984$ ) revealed in the ESR spectra of  $\alpha$ -cellulose and holocellulose extracted from coir pith after Cr(VI) adsorption, while the Cr(III) signal exhibited in the ESR spectra of lignin adsorbed Cr(VI). These results suggest that in Cr(VI) adsorption, the reduction process from Cr(VI) to Cr(V) should be occurred at the cellulose part of coir pith, and that from Cr(VI) to Cr(III), at lignin part of coir pith.

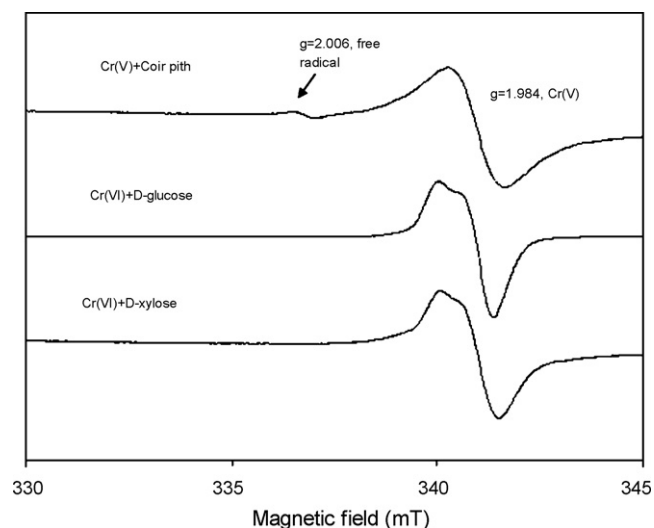
Generally, Cr(V) is unstable, but it could be observed in the ESR spectra of  $\alpha$ -cellulose and holocellulose extracted from coir pith suggesting that the intermediate Cr(V) may be bound with glucose [18] composing in cellulose resulted in the Cr(V) complex is stable. To investigate that glucose constituents in cellulose may be involved in the Cr(V) complex, ESR spectra of D-glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) adsorbed Cr(VI) was measured (Fig. 4). The results show that ESR spectra of D-glucose adsorbed Cr(VI) exhibited the signal with  $g = 1.984$ , Cr(V) that similar to ESR spectra of cellulose



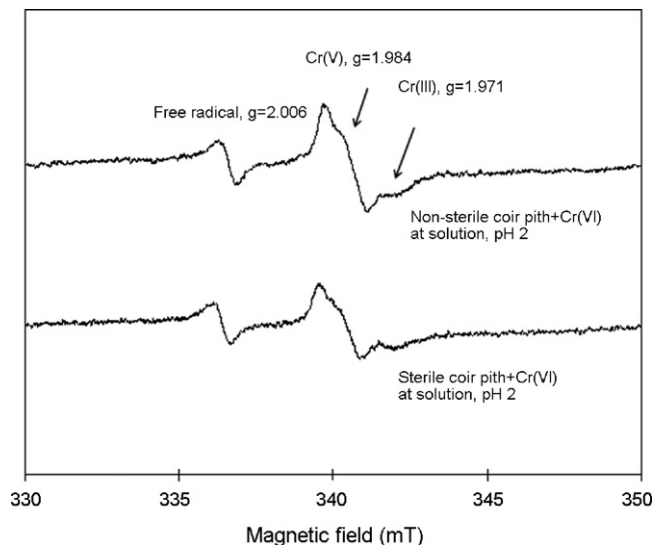
**Fig. 3.** ESR spectra of various adsorbents adsorbed Cr(VI) at solution pH 2 (conditions: Cr(VI) concentration =  $990 \text{ mg l}^{-1}$  contact time 18 h,  $30^\circ \text{C}$ , dosage = 2% w/v).

adsorbed Cr(VI). Thus, it confirmed that glucose in cellulose could be bound with Cr(V). Cr(III) was also not revealed on the surface of either holocellulose or  $\alpha$ -cellulose. This indicates that the reduction of Cr(VI) to Cr(III) had not occurred due to the fact that the electron supply for the reducing of Cr(VI) to Cr(III) is not enough. In addition, pentosan is also the composition in coir pith about 16.2% (data not shown). Xylose ( $\text{C}_5\text{H}_{10}\text{O}_5$ ) is the main component in pentosan. Therefore, xylose was used as adsorbents for the representative of the pentosan in coir pith for ESR experiment. As seen in Fig. 4, the results showed that the Cr(V) revealed in the xylose adsorbed Cr(VI). This indicates that the reduction of Cr(VI) to Cr(V) should also occur. Therefore, xylose and holocellulose and  $\alpha$ -cellulose are involved in the reduction of Cr(VI) to Cr(V) in coir pith.

The ESR spectra of lignin after Cr(VI) adsorption at solution pH 2 (Fig. 3), showed the signal of Cr(III) with  $g = 1.971$  and free radical with  $g = 2.006$ . The presence of Cr(III) signal in the ESR spectra of lignin indicates that the reduction from Cr(VI) to Cr(III) should occur in lignin surface after Cr(VI) adsorption. Generally, the reduction of Cr(VI) to Cr(III) requires a large amount of protons and electrons



**Fig. 4.** ESR spectra of D-glucose and D-xylose adsorbed Cr(VI) (conditions: Cr(VI) concentration =  $990 \text{ mg l}^{-1}$ , solution pH 2, contact time 18 h,  $30^\circ \text{C}$ ).



**Fig. 5.** ESR signal sterile coir pith and non-sterile coir pith adsorbed Cr(VI) (conditions: Cr(VI) concentration =  $990 \text{ mg l}^{-1}$ , solution pH 2, contact time 18 h,  $30^\circ \text{C}$ , dosage = 2% w/v).

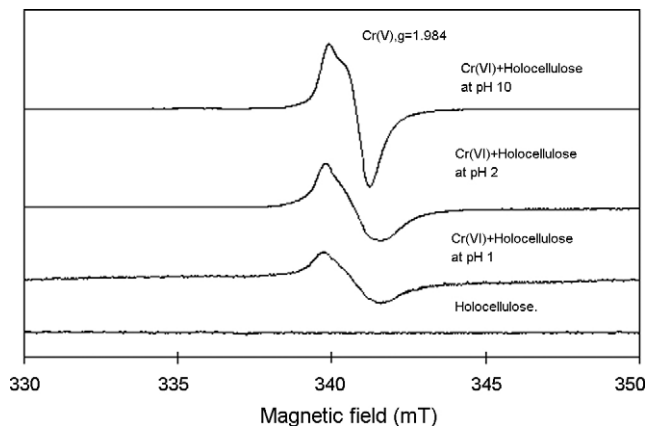
[19]. Therefore, the reduction from Cr(VI) to Cr(III) could occur due to the fact that the hydroxyl groups [20] and carbonyl groups [21] contained in lignin play a role as electron donor for the reduction reaction. The reduced Cr(III) on the lignin surface may be bound with carbonyl (C=O) and methoxy group (O-CH<sub>3</sub>) in lignin structure through a coordinate covalent bound [13]. Therefore, the Cr(III) signal on the lignin was observed by ESR.

From literature reviews reported that the appearance of Cr(V) is a known intermediate product during the reduction of Cr(VI) to Cr(III) by various plants, algae and bacteria that are living organisms [7]. Howe et al. [5] reported that those ESR spectra on subterranean clover plant adsorbed Cr(VI) revealed the presence of Cr(III) with both the low and high concentration Cr(VI) sorption and intermediate Cr(V), Cr(IV) with the high concentration. However, Cr(V) signal could be observed in coir pith adsorbed Cr(VI) as shown in Fig. 5, which is different from other research studied. Therefore, the confirmation for coir pith which is a non-living biomass was sterilized by autoclave at  $121^\circ \text{C}$  for 2 h. The comparison of ESR spectra between sterile coir pith and non-sterile coir pith were presented in Fig. 5. The results indicate that the ESR signal for non-sterile coir pith and sterile coir pith at solution pH 2 is not different. The Cr(V) signals were exhibited both in non-sterile coir pith and sterile coir pith adsorbed Cr(VI) at solution pH 2.

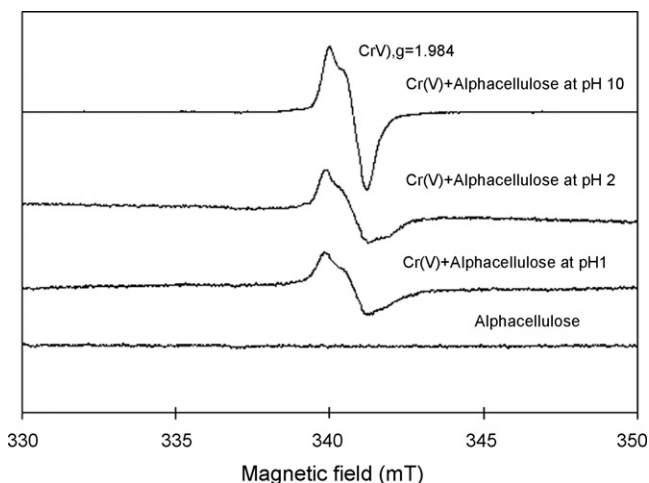
### 3.3. ESR of Cr(VI) adsorption by holocellulose, $\alpha$ -cellulose and lignin extracted from coir pith at various solution pH

The ESR spectra of Cr(VI) adsorbed on holocellulose and  $\alpha$ -cellulose extracted from coir pith at various solution pH were shown in Figs. 6 and 7, respectively. The results showed that the ESR spectra of holocellulose and  $\alpha$ -cellulose adsorbed Cr(VI) at solution pH 1, 2 and 10 exhibited the ESR signals with  $g = 1.984$  for Cr(V). The presence of Cr(V) indicated that Cr(VI) adsorbed on cellulose was reduced to Cr(V). In addition, the results showed that the signal intensity of Cr(V) at solution pH 10 is higher than pH 1 and 2 due to the fact that the Cr(VI) species in solution are different. The species of Cr(VI) in the high solution pH is  $\text{CrO}_4^{2-}$  while the form of  $\text{Cr}_2\text{O}_7^{2-}$  is the predominant in the low solution.

Fig. 8 showed the ESR of Cr(VI) adsorbed on lignin extracted from coir pith at various solution pH. The Cr(III) signal with  $g$  value = 1.971 was observed in the ESR spectra of lignin adsorbed Cr(VI) at solution

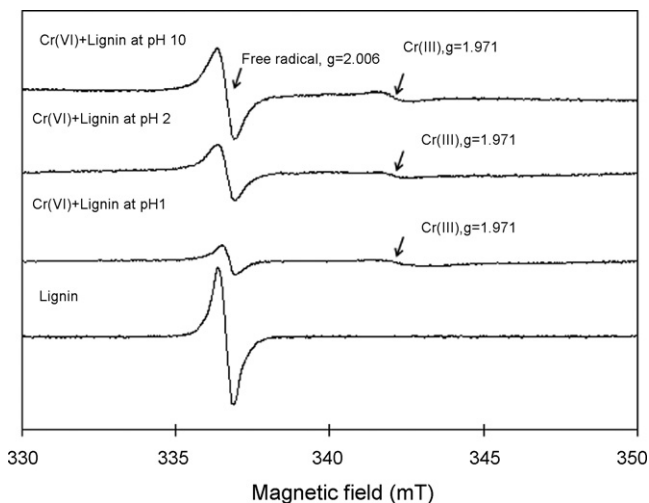


**Fig. 6.** ESR spectra of holocellulose adsorbed Cr(VI) at various solution pH.



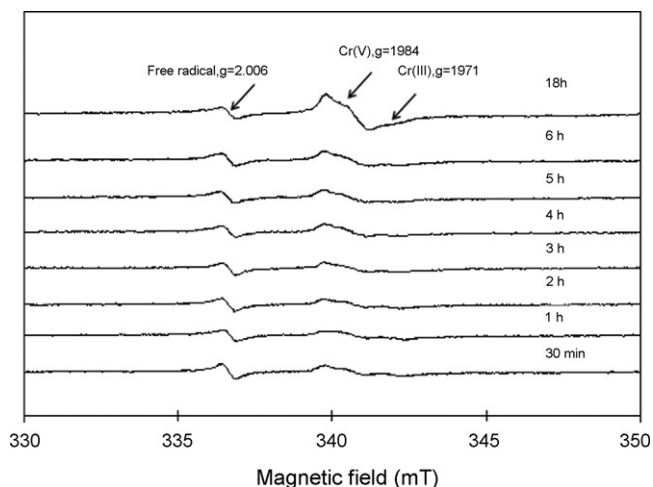
**Fig. 7.** ESR spectra of alphacellulose adsorbed Cr(VI) at various solution pH.

pH 1, 2 and 10. This indicated that the Cr(VI) adsorbed on lignin was reduced to Cr(III). However, the signal intensity of Cr(III) at solution pH 10 was more clearly observed than pH 1 and 2. This explained that the precipitation of  $\text{Cr}(\text{OH})_3$  occurred at high solution pH (pH 10).



**Fig. 8.** ESR spectra of lignin adsorbed Cr(VI) at various solution pH.





**Fig. 9.** ESR spectra of coir pith adsorbed Cr(VI) at solution pH 2 under various contact time.

### 3.4. ESR of Cr(VI) adsorption at various time

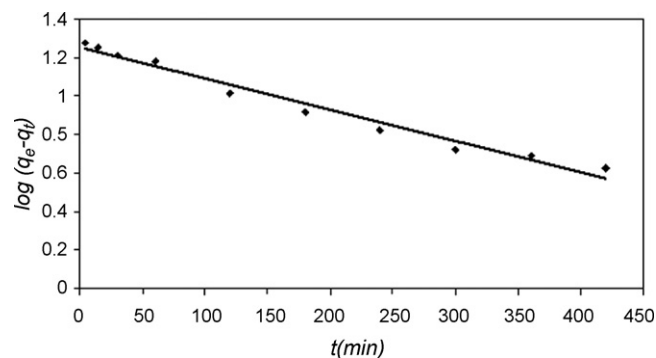
The ESR signals of coir pith adsorbed chromium in various contact time were shown in Fig. 9. The Cr(V) signal ( $g = 1.984$ ), Cr(III) ( $g = 1.971$ ) and free radical ( $g = 2.006$ ) were revealed in coir pith and that the signal intensity of Cr(V) was gradually increased with time up to 18 h, while the Cr(III) was almost constant. The signal intensity of Cr(V) increased with increasing the contact time due to the increase in the amounts of Cr(VI) adsorbed on coir pith. This led to the increase in the reduction of Cr(VI) to Cr(V) in cellulose part of coir. The amounts of Cr(VI) adsorption by coir pith were 11.22 and 33.47  $\text{mg g}^{-1}$  for 30 min and 18 h, respectively.

### 3.5. Adsorption kinetics

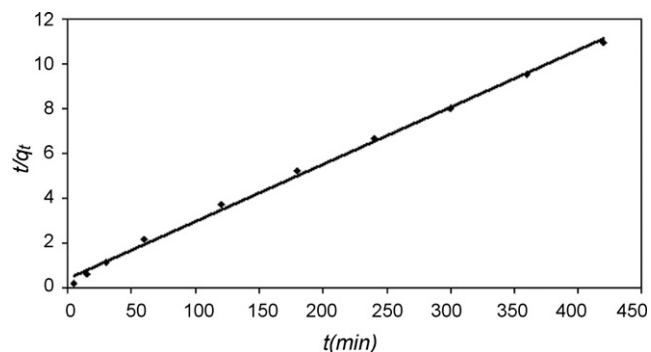
The adsorption kinetics of Cr(VI) adsorption on coir pith can be determined by the pseudo first order and pseudo second order model. The pseudo first order model is presented by the Lagergren equation as follows [22]:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (1)$$

where  $q_t$  and  $q_e$  are the amounts of Cr(VI) adsorbed ( $\text{mg g}^{-1}$ ) at any time  $t$  and at equilibrium, respectively;  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant of the pseudo first order adsorption. The values of  $q_e$  and  $k_1$  can be determined from the intercept and slope of the plot of  $\log(q_e - q_t)$  versus  $t$  (Fig. 10), respectively, and are listed in Table 1. The pseudo second order model according to Ho and Mackay [23] is expressed as:  $(2) \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$  where  $k_2$  ( $\text{g}^{-1} \text{mg}^{-1} \text{min}^{-1}$ ) is the rate constant of the pseudo second order model. The plot of  $t/q$  versus  $t$  is presented in Fig. 11. The values of  $q_e$  and  $k_2$  can be calculated from the slope and intercept of the plot, respectively, and are shown in Table 1. The pseudo second order model shows a better fitting model than the pseudo first order model because of the higher coefficient correlation ( $r^2$ ). In addition, it can be seen from Table 1 that the theoretical value of  $q_e$  calculated by pseudo second order model is quite close to the experimental values, while  $q_e$



**Fig. 10.** Pseudo first order kinetic plots for Cr(VI) adsorption by coir pith (conditions: Cr(VI) 990  $\text{mg l}^{-1}$ , temperature 30 °C, solution pH 2, dosage = 2% w/v, particle size < 75  $\mu\text{m}$ ).



**Fig. 11.** Pseudo second order kinetic plots for Cr(VI) adsorption by coir pith (conditions: Cr(VI) 990  $\text{mg l}^{-1}$ , temperature 30 °C, solution pH 2, dosage = 2% w/v, particle size < 75  $\mu\text{m}$ ).

calculated by pseudo first order is different from the experimental value. Thus, it is suggested that the adsorption kinetics of Cr(VI) on coir pith are appropriately described by the pseudo second order model. A similar phenomenon has been observed in Cr(VI) adsorption by used tyres and sawdust [24] and ethylenediamine modified rice hull [25]. The adsorption kinetics fitted well with the pseudo second order model. This suggested that the adsorption of Cr(VI) on coir pith involved a chemisorption process [25,26].

### 3.6. Desorption study

In batch studies, the desorption experiments were studies using 2 M  $\text{HNO}_3$  and 1 M NaOH as eluents. The Cr(VI) desorption with 1 M NaOH was 15.63%. In addition, Cr(III) can be desorbed with 2 M  $\text{HNO}_3$  approximately 71.48%. This indicated the high percentages of Cr(III) desorption with 2 M  $\text{HNO}_3$ . However, Cr(III) desorption is not reach 100% (only 71.48%) although the 2 M  $\text{HNO}_3$  is very strong acidic solution for desorption. It suggested that Cr(V) bound with glucose in cellulose part of coir pith (data from ESR experiments) is quite stable. Therefore, it cannot be desorbed in the solution. These results confirmed that Cr(VI), Cr(V) and Cr(III), exit in coir pith. The desorption data indicated that percentage of Cr(VI), Cr(V) and Cr(III) in coir pith were 15.63%, 12.89% and 71.48%, respectively.

**Table 1**

Kinetic parameters for Cr(VI) adsorption by coir pith (conditions: Cr(VI) 990  $\text{mg l}^{-1}$ , temperature 30 °C, solution pH 2, dosage = 2% w/v, particle size < 75  $\mu\text{m}$ )

Model	$q_{e(\text{exp})}$ ( $\text{mg g}^{-1}$ )	$q_{e(\text{cal})}$ ( $\text{mg g}^{-1}$ )	Rate constant	$r^2$
Pseudo first order	42.71	17.827	$k_1$ ( $\text{min}^{-1}$ ), 0.00368	0.9721
Pseudo second order	42.71	39.21	$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ ), 0.00159	0.9972

#### 4. Conclusions

The ESR spectra of coir pith adsorbed Cr(VI) at solution pH 2 exhibited both Cr(V) and Cr(III) signals, while ESR spectra of lignin extracted from coir pith revealed Cr(III) signal. On the other hand, ESR signal of Cr(V) was observed in  $\alpha$ -cellulose and holocellulose extracted from coir pith adsorbed Cr(VI). These results suggested that there exist a couple of Cr(VI) adsorption sites, cellulose site with the reduction process from Cr(VI) to Cr(V) and lignin site with that from Cr(VI) to Cr(III). The Cr(V) signal exhibited in ESR of  $\alpha$ -cellulose and holocellulose might be bound with glucose in cellulose part of coir pith. In addition, xylose which is the main in pentosan part of coir pith, indicated that it is involved in form complex with Cr(V) on coir pith. The adsorption kinetic for Cr(VI) adsorption on coir pith fitted well with pseudo second order model, indicating that the mechanism of Cr(VI) adsorption on coir pith involved the chemisorption process. From ESR and desorption experiments confirmed that Cr(VI), Cr(V) and Cr(III), exist in coir pith after Cr(VI) adsorption. The desorption data indicated that percentage of Cr(VI), Cr(V) and Cr(III) in coir pith were 15.63%, 12.89% and 71.48%, respectively. The percentage of Cr(VI) adsorption on lignin extracted from coir pith has quite high (84.63% at solution pH 2) when compared to the holocellulose (16.92% at solution pH 2) and  $\alpha$ -cellulose (6.94% at solution pH 2).

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#### References

- [1] E. Malkoc, Y. Nuhoglu, Y. Abali, Cr(VI) adsorption by waste a corn of *Quercus ithaburensis* in fixed beds: prediction of breakthrough curves, Chem. Eng. J. 119 (2006) 61–68.
- [2] G.Q. Chen, G.M. Zeng, X. Tu, C.-G. Niu, C.-H. Application of a by-product of *Lentinus edodes* to the bioremediation of chromate, J. Hazard. Mater. B135 (2006) 249–255.
- [3] A. Verma, S. Chakraborty, J.K. Basu, Adsorption study of hexavalent chromium using tamarind hull-based adsorbents, Sep. Purif. Technol. 50 (2006) 336–341.
- [4] N.R. Bishnoi, M. Bajaj, N. Sharma, A. Gupta, Adsorption of Cr(VI) on activated rice husk carbon and activated alumina, Bioresour. Technol. 91 (2004) 305–307.
- [5] J.A. Howe, R.H. Loeppert, V.J. Derose, D.B. Hunter, P.M. Bertsch, Localization and speciation of chromium in subtterranean clover using XRF, XANES, and EPR Spectroscopy, Environ. Sci. Technol. 37 (2003) 4091–4097.
- [6] C.M. Lytle, F.W. Lytle, N. Yang, J.H. Qian, D. Hansen, A. Zayed, N. Terry, Reduction of Cr(VI) to Cr(III) by wetland plants: potential in situ heavy metal detoxification, Environ. Sci. Technol. 32 (1998) 3087–3093.
- [7] T.L. Kalabegishvili, N.Y. Tsibakhashvili, H.Y.N. Holman, Electron spin resonance study of chromium (V) formation and decomposition by basalt-inhabiting bacteria, Environ. Sci. Technol. 37 (2003) 4678–4684.
- [8] R. Codd, P.A. Lay, N.Y. Tsibakhashvili, T.L. Kalabegishvili, I.G. Murusidze, H.Y.N. Holman, Chromium (V) complexes generated in *Arthrobacter oxydans* by simulation analysis of EPR spectra, J. Inorg. Biochem. 100 (2006) 1827–1833.
- [9] J.G. Parson, M. Hejazi, K.J. Tiemann, J. Henning, J.L. Gardea-Torresdey, An XAS study of the binding of copper (II), zinc (II), chromium (III) and chromium (VI) to hops biomass, Microchem. J. 71 (2002) 211–219.
- [10] M.J. Hu, Y.L. Wei, Y.W. Yang, J.F. Lee, X-ray absorption spectroscopy study of chromium recovered from Cr(VI)-containing water with rice husk, J. Phys.: Condens. Matter. 16 (2004) 3474–3478.
- [11] D. Park, Y.S. Yun, J.H. Jo, J.M. Park, Mechanism of hexavalent chromium removal by dead fungal biomass of *Aspergillus niger*, Water Res. 39 (2005) 533–540.
- [12] J.L. Gardea-Torresdey, K.J. Tiemann, V. Armendariz, L. Bess-Obert, R.R. Chianelli, J. Rios, J.G. Parsons, G. Gamez, Characterization of Cr(VI) binding and reduction to Cr(III) by the agricultural byproducts of *Avena monida* (Oat) biomass, J. Hazard. Mater. B80 (2000) 175–188.
- [13] P. Suksabye, P. Thiravetyan, W. Nakbanpote, S. Chayabutra, Chromium removal from electroplating wastewater by coir pith, J. Hazard. Mater. 141 (2007) 637–644.
- [14] Technical Association of the Pulp and Paper Industry, TAPPI test method, TAPPI T 222 om-88, USA.
- [15] Technical Association of the Pulp and Paper Industry, TAPPI test method, TAPPI T 203 om-93, USA.
- [16] B.L. Browning, Method of Wood Chemistry, John Wiley and Sons, New York, 1967, pp. 394–396.
- [17] M. Krumpolc, J. Rocek, Sodium bis[2-ethyl-2-hydroxybutyrate(2-)]-oxochromate(V), Inorg. Synth. 20 (1980) 63–65.
- [18] S. Signorella, R. Lafarga, V. Daier, L.F. Sala, The reduction of Cr(VI) to Cr(III) by  $\alpha$  and  $\beta$  anomers of D-glucose in dimethyl sulfoxide: a comparative kinetic and mechanistic study, Carbohydr. Res. 324 (2000) 127–135.
- [19] D. Park, Y.-S. Yun, J.M. Park, Reduction of hexavalent chromium with the brown seaweeds *Ecklonia* biomass, Environ. Sci. Technol. 38 (2004) 4860–4864.
- [20] S. Babel, T.A. Kurniawan, Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan, Chemosphere 54 (2004) 951–967.
- [21] Y. Nakano, K. Takeshita, T. Tsutsumi, Adsorption mechanism of hexavalent chromium by redox within condensed-tannin gel, Water Res. 35 (2000) 496–500.
- [22] E. Malkoc, Y. Nuhoglu, Potential of tea factory for chromium (VI) removal from aqueous solutions: thermodynamic and kinetic studies, Sep. Purif. Technol. 57 (2007) 291–298.
- [23] Y.S. Ho, G. Mackay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.
- [24] N.K. Hamadi, X.D. Chen, M.M. Farid, M.G.Q. Lu, Adsorption kinetics for the removal of chromium (VI) from aqueous solution by adsorbents derived from used tyre and sawdust, Chem. Eng. J. 84 (2001) 95–105.
- [25] P.L. Tang, C.K. Lee, K.S. Low, Z. Zainal, Sorption of Cr(VI) and Cu(II) in aqueous solution by ethylenediamine modified rice hull, Environ. Technol. 24 (2003) 1243–1251.
- [26] M.X. Loukidou, A.I. Zouboulis, T.D. Karapantsios, K.A. Matis, Equilibrium and kinetic modeling of chromium (VI) biosorption by *Aeromonas caviae*, Colloid Surf. A: Physicochem. Eng. Aspects 242 (2004) 93–104.