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Adsorption of hexavalent chromium onto sisal pulp/polypyrrole composites

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Abstract. Sisal pulp/polypyrrole composites (SP/PPy) utilized for the removal of hexavalent chromium [Cr(VI)] from wastewater, were prepared via in-situ chemical oxidation polymerization approach. The structure and morphology of the SP/PPy were analyzed by polarizing optical microscopy (POM), field-emission scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS), the results indicated SP could be efficient dispersion of PPy. The hexavalent chromium adsorption results indicate adsorption capacity of the SP/PPy were dependent on the initial pH, with an optimum pH of 2.0. The sorption kinetic data fitted well to the pseudo-second order model and isotherm data fitted well to the Langmuir isotherm model. The maximum adsorption capacity determined from the Langmuir isotherm is 336.70 mg/g at 25° C.

1. Introduction

Chromic (Cr) compounds are widely used in chemical industry, such as electroplating, metallurgy, electronics, industrial dyeing, leather tanning, etc. Consequently, large amounts of industrial wastewater containing Cr(VI) are produced. The direct discharge of waste-water has serious adverse effects on aquatic life and human health. Chromium generally exists in trivalent and hexavalent oxidation states. Cr(VI) compounds are more toxic due to their carcinogenicity. The World Health Organization (WHO) has proposed regulations on the limits of Cr(VI) in groundwater and drinking water, which are 0.1 mg/L and 0.05 mg/L, respectively. Hence, wastewater containing Cr(VI) must be strict treated before being discharged. Commonly used methods for the removal of metal ion from water include chemical precipitation, electrochemical reduction method[1,2], ion exchange[3,4], membrane separation[5,6], complexation and adsorption[7]. Among these methods, adsorption is a promising alternative because it is simple, efficient and economic.

Polypyrrole (PPy) containing nitrogen have shown high binding affinity to metal ion. Moreover, PPy are easily coating on different substrates through in-situ polymerization of pyrrole, and their coatings can be exchanged with ambient ions under solution states, this properties render PPy promising candidates as metal ion absorption materials. Many sorbing materials based PPy have been reported for Cr(VI) removal. For examples, montmorillonite /PPy[8], sepiolite fiber/PPy[9], halloysite/PPy nanotube clay[10] and polyaniline/PPy [11]. The maximum of adsorption capacity (qm) of bamboo-like PPy nanotubes[12], PPy-graphene oxide composites[13] and polyacrylonitrile/PPy core-shell nanofiber membrane[14] for Cr(VI) adsorption were 482.60 mg/g, 625 mg/g and 61.80 mg/g, respectively. However, for practical utility there is still a requirement for new materials showing a highly removal capacity.
The development of PPy based toxic metal ions absorption materials are of both scientific and technological interest. However, an obstacle is the notorious aggregation of PPy. This problems must be properly tackled, because of aggregation highly effect on absorptivity. In order to solve aggregation problem and enhance the adsorption capacity, various chemical, physical, and engineering approaches have been taken to frustrate PPy aggregation.

In this paper, we utilized renewable and biodegradable sisal pulp, prepared SP/PPy via a simple in-situ chemical oxidation polymerization. PPy well distributed on SP surface, and the SP/PPy with large surface area and enhance adsorption capacity due to the microstructures and good dispersion of SP.

2. Experimental details

2.1.Materials
Sisal fiber was obtained from Guangxi Sisal Group Co. Ltd. pyrrole was vacuum distillated before used. Other commercially available reagents were used without further purification. Sisal pulp(SP) was prepared following the sulfate digestion process[15]. A stock Cr(VI) solution was prepared by dissolving a known amount of K2Cr2O7 with deionized water. The pH of the solution was regulated by HCl and NaOH solution.

2.2.Preparation of SP/PPy.
SP/PPy were prepared by an in-situ chemical oxidation polymerization approach, as follows: 1000 mg of dry SP, 926 mg of FeCl3•6H2O and 100 mL of 0.5 M HCl were placed into a 500 mL three neck round bottom flask and stirred 30 min; 105 μL pyrrole was dropsies at room temperature under and continually stirred for 5 h. After the reaction, the solid was collected, and rinsed with deionized water and ethanol alternately until the filtrate was clear, dried at 55º C for 24 h. The molar ratio of pyrrole to FeCl3•6H2O was 1:2.3. Different pyrrole concentrations were denoted as SP/PPy-x (x was pyrrole the concentration, g/L). The preparation process is illustrated in Figure 1.

![Figure 1. Preparation of SP/PPy.](image)

2.3. Adsorption studies
Effects of pH. The effects of the initial pH on Cr(VI) adsorption were investigated in the range of 2~10. 20 mg SP/PPy were added to 20 mL of solution with 100 mg/L, after 24 h, the adsorbent was separated from the solution by filtration, and the filtrate was analyzed by UV-vis spectroscopy.

Kinetic study and adsorption isotherms. An amount of 100 mL of different Cr(VI) solutions (initial concentrations from 100~400 mg/L) and 100 mg SP/PPy were added until reaching the adsorption equilibrium at room temperature (25º C). Time was taken for the samples to be analyzed. The concentrations of the Cr(VI) samples were analyzed by spectrophotometry using 1,5-diphenylcarbazide as the complexing agent at the wavelength of 540 nm (GB 7467-87). At the end of the experiments, the adsorbent was separated from the solution by filtration. The removal and adsorption capacity for Cr(VI) were obtained as follows:

\[
\% \text{ of removal} = \frac{C_0 - C_t}{C_0} \times 100%
\]

\[
q_t = \frac{(C_0 - C_t)}{m} \times V
\]

\[
q_e = \frac{(C_0 - C_e)}{m} \times V
\]

Where \(C_0\), \(C_t\), and \(C_e\) were the initial concentration, the concentration at t and equilibrium concentrations (mg•L⁻¹) of Cr(VI), respectively; \(q_t\) and \(q_e\) were the adsorption capacity at t and equilibrium (mg•g⁻¹); m is the mass of adsorbent (mg); and V is the initial volume (mL) of the Cr(VI) solution.

The surfaces of SP/PPy were observed using a polarized optical microscope (POM; ECLPSE E200, Japan). The morphologies of composites were characterized by field-emission scanning electron microscopy (FE-SEM; JSM6380-LV, Japan) and the elemental components were characterized using distribution energy dispersive X-ray analysis (EDS; JSM-5600LV, Japan). The concentrations of Cr(VI) ions in the aqueous solutions were...
measured by UV-vis spectroscopy (TU-1901; Beijing). X-ray photoelectron spectroscopy (XPS; ESCALAB 250XI, USA) equipped with an Al Kα radiation source was employed to determine the element of SP/PPy.

3. Results and discussion

3.1. Morphology of SP/PPy

**Figure 2** shows SEM micrographs of SP, PPy, SP/PPy-7.0 and Cr@SP/PPy-7.0 (SP/PPy-7.0 after Cr(VI) adsorption). **Figure 2** (a) shows the pure SP had an uneven surface with wrinkles and were covered with flocculent fiber. **Figure 2** (b) shows the PPy had a cauliflower-like structure [16] with a particle size of ~1 μm. **Figure 2** (c) show a PPy layer was adhered to the surfaces of the SP/PPy-7.0 with diameters of ~100 nm, indicating that the flocculent fiber around the SP acted as a template while the pyrrole was polymerized [9,17]. This perhaps that PPy carried positive charges on the N atoms when it propagated in the reaction medium. Due to the large amount of -OH groups and the negative charges on the SP, positively charged PPy was oriented on the fibrous surface of the SP, and the SP/PPy was formed during oxidation polymerization. After Cr(VI) absorption, the micrographs of the Cr@SP/PPy-7.0 composites hardly changed, as shown in **Figure 2** (d).

**Figure 2.** SEM images of (a)SP; (b)PPy; (c)SP/PPy-7.0; (d)Cr@SP/PPy-7.0.

**Figure 3.** POM images of (a) SP; (b) SP/PPy-1.0; (c) SP/PPy-5.0; (d) SP/PPy-7.0.

**Figure 3** shows POM images of the SP and SP/PPy composites. The SP showed a typical birefringence colorful pattern under the polarizing microscope (**Figure 3** (a)) because of their crystalline. Increase of pyrrole content, the birefringence colorful pattern of SP/PPy fade away (**Figure 3** (b) ~ (d)), especially, SP/PPy-5.0 and SP/PPy-7.0, the displayed views are dark and the birefringence have been completely disappeared [18]. This results indicates that PPy have been effective coating on sisal pulp surface. The average diameter and lengths of the SP and SP/PPy were 15 μm and 200 to 300 μm.

3.2. Batch adsorption studies

The concentration and pH of the aqueous solution greatly affected the Cr(VI). When pH<1, Cr(VI) mainly existed as H₂CrO₄. When 2<pH<6, Cr(VI) was converted into HCrO₄⁻ (main) and Cr₂O₇²⁻. When 6<pH<8, Cr(VI) existed as Cr₂O₇²⁻ and CrO₄²⁻. When pH>8, Cr(VI) existed as CrO₄²⁻ [19].

The pH of the solution was an important factor for metal ion sorption, because it not only affected the diffusion of dichromate ions but also the surface charge of the adsorbent. Moreover, it may have participated in the speciation of the adsorbent during reaction [20]. **Figure 4** (a) shows the Cr(VI) removal efficiency with different adsorbents at various pH values. The figure shows that Cr(VI) removal with the SP/PPy and PPy were pH-dependent and optimum removal for both occurred at 2. The percentage of Cr⁶⁺ removal with the SP/PPy and the PPy were 99.2% and 55.6%, respectively. These values may have been due to the absorbents being protonated and the strong attraction between HCrO₄⁻ at a low pH level, resulting in the Cr(VI) being easily removed. As the pH increased, more OH⁻ competed with the HCrO₄⁻, resulting in a decrease of Cr(VI) removal [9,13,14]. Moreover, the adsorption capacity of Cr(VI) with the SP was very weak and pH-independent. The Cr(VI) adsorption was shown to be more successful with the SP/PPy than the PPy. This was probably due to the increase in the number of active sites because the SP of the SP/PPy acted as a support matrix material that effectively prevented the PPy from agglomerating during polymerization.

The SP/PPy prepared with different pyrrole concentrations showed different adsorption performances. **Figure 4** (b) shows the Cr(VI) removal efficiency of the SP/PPy prepared with various pyrrole concentrations.
It was observed that the removal efficiency increased from 33.7% to 97.9% as the pyrrole concentration increased from 1.0 to 7.0 g/L after 24 h absorption. The increase in performance as the pyrrole concentration increased was probably due to an increased number of active sites provided by the SP/PPy. However, when the monomer concentration was more than 7.0 g/L, the removal efficiency decreased sharply to 64.5% [21]. It could have been the SP/PPy prone to agglomeration as the pyrrole concentration increased resulted in a reduction of the density of effective adsorption sites for Cr(VI) removal. In summary, the SP/PPy-7.0 showed the best adsorption capacity for Cr(VI) removal.

The dosage of sorbent is an important parameter for metal ion removal, so the amount of SP/PPy-7.0 was investigated to establish the appropriate value for a given initial concentration of heavy metal ion solution. The results illustrated in Figure 4 (c) show how the different SP/PPy-7.0 amounts affected Cr(VI) removal in 20 mL of 200 mg/L solution. The removal efficiency increased from 32.1% to 98.0% as the sorbent dosage increased from 5.00 mg to 20.00 mg. This was because the increased amount of adsorbent provided more adsorption sites for Cr(VI) removal. But if the amount of SP/PPy-7.0 was increased to more than 20 mg/20 ml, the Cr(VI) removal began to slow. This suggested that the optimal amount of adsorbent was 20 mg/20 ml for the treatment of a solution with an initial Cr(VI) concentration of 200 mg/L.

![Figure 4. Effects of pH(a), pyrrole concentration(b), and dose of SP/PPy-7.0(c) on Cr(VI) adsorption.](image)

### 3.3 Adsorption kinetics

To study the adsorption process of Cr(VI), the adsorption kinetics of the SP/PPy-7.0 with different initial concentrations of Cr(VI) were studied (show in Figure 5 (a)). It was observed that when the initial Cr(VI) concentration increased from 100 to 400 mg/L, the adsorption capacity of the SP/PPy also increased. When the initial concentration of Cr(VI) was 100 mg/L, the absorb equilibrium time was 12 h. It was extended to 32 h with the initial concentration at 200 mg/L. A higher initial concentration of Cr(VI) caused longer adsorption equilibrium time. The equilibrium adsorption capacity was 100.37, 200.33, 291.01, and 335.00 mg•g⁻¹ when the initial concentrations were 100, 200, 300, and 400 mg/L, respectively.

The kinetic data were further interpreted using the pseudo-second order kinetic models [22], which can be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{t}{q_f}$$

(4)

where \(K_2\) was the rate constant (g mg⁻¹•min⁻¹) of the pseudo-second-order kinetic model.

The pseudo-second order rate parameters for chromium sorption with four initial concentrations were calculated from the linear plots of \(t/q_t\) versus \(t\) (Figure 5 (b)). The values of the correlation coefficients \((R^2)\) were >0.99, and calculated equilibrium capacity values were consistent with the experimental values, which indicated that the kinetics of sorption of Cr(VI) ions with the SP/PPy followed the pseudo-second order mechanism[16,23]. In other words, this adsorption process was chemisorption involving valency forces through the sharing or exchange of electrons between the SP/PPy and Cr(VI) ions as covalent forces and ion exchanges[22,24,25].

### 3.4 Adsorption isotherm

To determine the capacity parameters of Cr(VI) adsorption on the SP/PPy-7.0, adsorption isotherm was obtained at 25 °C, 35 °C, 45 °C. Figure 5 (c) illustrates that the adsorption capacity of the SP/PPy-7.0 increased with the increasing temperature. And the adsorption equilibrium data was fitted with a linearized Langmuir model (5), which is shown in Figure 5 (d). The expression of the Langmuir model is as follows:

$$\frac{C}{q_e} = \frac{1}{q_m} + \frac{C}{q_m}$$

(5)
where $q_m$ is the maximum adsorption capacity (mg/g) and $b$ is the adsorption equilibrium constant (L/mg). Then, $q_m$ and $b$ can be calculated, as shown in Figure 5 (d) and listed in Table 1.

![Figure 5](image_url)

**Table 1.** Parameters of the Langmuir isotherm model

| T (K) | $b$ (mg/L) | $q_m$ (mg/g) | $R^2$ |
|-------|------------|--------------|-------|
| 298   | 1.4854     | 326.7974     | 0.9988|
| 308   | 5.7724     | 358.4229     | 0.9998|
| 318   | 109.8423   | 377.3585     | 1.0000|

The Langmuir adsorption isotherm model was assumed as monolayer adsorption onto the surface of the adsorbent and there was no interaction between the adjacent adsorption sites. The values of the correlation coefficients ($R^2$) were $>0.999$, indicating that the equilibrium data of the Cr(VI) removal on the SP/PPy-7.0 was as described by the Langmuir isotherm. The maximum adsorption capacities calculated from the Langmuir isotherm of the SP/PPy-7.0 were 336.80, 358.42 and 377.36 mg/g at 25 °C, 35 °C and 45 °C, respectively. Compared to the other adsorbents listed in Table 2, SP/PPy composites have relatively high adsorption capacity.

**Table 2.** Adsorption performances of various adsorbents and SP/PPy-7.0.

| Adsorbent                  | $q_m$ (mg/g) | pH  | T/K | Ref. |
|----------------------------|--------------|-----|-----|------|
| Glycine doped PPy          | 217.39       | 2.0 | 298 | [26] |
| PPy-sepiolite nanofibers   | 302.00       | 2.0 | 298 | [9]  |
| Bamboo-like PPy nanotubes  | 482.60       | 3.0 | -   | [12] |
| PPy-PANI nanofiber         | 227.00       | 2.0 | 298 | [11] |
| PPy/Fe$_3$O$_4$ nanocomposites | 169.49  | 2.0 | 298 | [27] |
| PPy/MMT nanocomposites     | 166.70       | 2.0 | 303 | [8]  |
| PAN/PPy nanofiber mat      | 61.80        | 2.0 | 298 | [14] |
| SP/PPy composites          | 334.45       | 2.0 | 298 | this|
These results indicated SP/PPy-7.0 have important and potential application in environmental protection field due to their excellent adsorption capacity, simple procedure, low cost, and easy to separate from the solution after the adsorption process.

3.5 EDS and XPS of SP/PPy before and after Cr(VI) adsorption

Energy dispersive X-rays (EDS) were used to analysis the elemental constituents of the SP/PPy before and after the adsorption of Cr(VI). As shown in Fig.6., there were obvious intense Cr peaks after the adsorption, while there weren’t observed before the adsorption. This results clearly indicated that Cr species had been efficient adsorbed by the SP/PPy [8,13,16].

![Figure 6. EDS spectra of SP/PPy-7.0: (a) Before and (b) After Cr(VI) adsorption.](image)

![Figure 7. (a) XPS survey spectra of SP/PPy-7.0; (b) XPS Cr2p region of SP/PPy-7.0 after Cr(VI) adsorption.](image)

In order to study the adsorption mechanism, XPS was used to investigate the surface element composition of the SP/PPy before and after the adsorption. Figure 7 (a) shows the XPS survey spectra of the SP/PPy-7.0. It was observed that a new Cr element emerged on the SP/PPy-7.0 after the adsorption of Cr(VI) that was not observed before. Simultaneously, an increase in oxygen content was noted, while the signal of the Cl was significantly reduced after the Cr(VI) adsorption. The Cr(VI) ions most likely replaced the Cl ions on the SP/PPy during the Cr(VI) adsorption by anion exchange[28,29]. Figure 7 (b) shows the XPS Cr2p region of the SP/PPy-7.0 after the Cr(VI) adsorption. The significant bands appearing at the binding energies of 577.0 ~ 578.0 and 586.0 ~ 588.0 eV appeared after the Cr(VI) adsorption, which corresponded to Cr 2p1/2 and Cr 2p3/2, respectively[30]. The Cr 2p3/2 can be split into two peak components with BEs of 576.48 eV and 578.09 eV, corresponding to Cr(III) and Cr(VI), respectively[30-32]. In summary, the Cr(VI) on the surface of the SP/PPy attributed to the anion-exchange of the PPy by replacing the doped Cl⁻ with either HCrO₄⁻ or Cr₂O₇²⁻. And the presence of Cr(III) was due to the reduction property of the PPy on the Cr(VI)[12,30].

4. Conclusions

SP/PPy were prepared via simple in-situ chemical oxidation polymerization approach. The adsorption of Cr(VI) on the SP/PPy depended on the initial pH, with an optimum pH of 2.0. Under the same conditions, the adsorption efficiency of SP, pure PPy and SP/PPy are 4%, 55.6% and 99.2%, respectively. This result indicates PPy could be more efficient absorption ability through SP dispersion. The interaction between the Cr(VI) and the SP/PPy-7.0 followed the pseudo-second order mechanism. The adsorption equilibrium data fitted well with the Langmuir isotherm model, maximum adsorption capacity up to 336.70 mg/g at 25 °C was achieved with the SP/PPy-7.0. To the best of our knowledge, SP/PPy are one of best absorption materials based PPy for removal Cr(VI) ions.

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