The adsorption ability of Cr(VI) on sawdust–polyaniline nanocomposite

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Abstract

The results of this study of sawdust–polyaniline nanocomposite synthesized by a chemical method for Cr(VI) treatment in the environment are presented. Cr(VI) adsorption on a composite was determined by colorimetry. The results showed that sawdust–polyaniline composite synthesized with an aniline : sawdust ratio equal to 0.5 had an adsorption degree of 21.4 mg g⁻¹ and adsorbed nearly 99% of the Cr(VI) after 2 h. The composite could be used for the adsorption of Cr(VI) from waste water. The Cr(VI) adsorption ability of the composite slightly depends on the pH value of the medium. The adsorption is fast during the first half hour and then the rate decreases.

Keywords: Sawdust, polyaniline, nanocomposite, Cr(VI)-adsorption

Classification number: 5.00

1. Introduction

Among the conducting polymers, polyaniline (PANi) has been the most interesting because of its many advantages. It has been used for different purposes: performance of rechargeable batteries [1, 2], preparation of sensors [3], protection of metals from corrosion [4], manufacture of electronic devices [5], etc. Furthermore, its preparation is very simple and cheap, and the product is stable in the environment. It is well known that PANi exists in three different oxidation states corresponding to different colour states, and among them only the emeraldine form is electrically conductive [6, 7].

If PANi exists in salt form, it is good at adsorbing Cr(VI) from solution because of the anion exchange between Cl⁻ and Cr₂O₇²⁻. It is also well known that Cr(VI) exists in HCrO₄⁻ form if the pH = 1, and thus the following reactions can occur:

\[ \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightarrow 2\text{HCrO}_4^- \]

\[ \text{PANi}/\text{Cl}^- + \text{HCrO}_4^- \rightarrow \text{PANi}/\text{HCrO}_4^- + \text{Cl}^- \]

From sawdust as a resource material and PANi, a new composite for the adsorption of Cr(VI) was synthesized [8]. It has been shown that Cr(VI) anions can be adsorbed onto the surface of the composite due to anion exchange through the PANi membrane. In this work, a similar nanocomposite was prepared directly by the chemical polymerization of aniline on the surface of sawdust. Its application for Cr(VI) adsorption will be discussed in detail.

2. Experimental

2.1. Synthesis procedure of sawdust–PANi composite

First, we poured 100 ml of 1 M HCl into a triangle glass vessel placed in an ice basin, adding an amount of sawdust under stirring and then 2.28 g of ammonium persulfate. Then aniline was added into the reaction solution in the aniline:sawdust ratio equal to 0.5 had an adsorption degree of 21.4 mg g⁻¹ and adsorbed nearly 99% of the Cr(VI) after 2 h. The composite could be used for the adsorption of Cr(VI) from waste water. The Cr(VI) adsorption ability of the composite slightly depends on the pH value of the medium. The adsorption is fast during the first half hour and then the rate decreases.
was measured by cyclic voltammetry (CV) by the two-point-electrode method on the electrochemical workstation IM6 (Zahner-Elektrik, Germany).

2.3. Cr(VI) adsorption

A solution of Cr(VI) (C_{Cr(VI)} = 53.5 mg l^{-1}, pH = 1) was prepared for the adsorption investigation. Eight triangle glass vessels were prepared, each containing 20 ml of K_{2}Cr_{2}O_{7} and 50 mg of sawdust–PANi composite with different ratios between the aniline and sawdust. The reaction solution was filtered after an adsorption time of 30 min to determine the remaining Cr(VI) by colorimetry. The best of the Cr(VI) adsorbing composites was chosen by studying the pH and adsorption time dependence of their adsorption ability.

3. Results and discussions

3.1. SEM analysis

In figure 1(a) it can be seen that the sawdust had a structural morphology like many bundles of chopsticks with a diameter of about 200–500 nm. However, it was not compact. After the fabrication of the sawdust–PANi composite, the sawdust chopsticks could not be observed any more, because of PANi coating onto their surface (figure 1(b)). The diameter of the sawdust–PANi composite was found to be about 50–70 nm.

3.2. IR-Analysis

Sawdust has a fibre structure and its main component is cellulose (C_{6}H_{10}O_{5})_{n}, which has a straight chain structure and very large molecule mass (1700 000–2400 000 unit C). Molecules of cellulose are formed from β-glucose sources, which bind together by C_{1} of a source with C_{4} of another one through the oxygen atom.

Comparing the IR-spectrum of the sawdust (figure 2) with that of the sawdust–PANi composite (figure 3), we observed a decrease in the intensity of the adsorption coefficient at wave numbers larger than 2500 cm^{-1}. However, the shift in the peaks is negligible.

3.3. Conductivity

The conductivity of PANi was determined through CV diagrams in figure 4. The higher slope has the CV line; the lower electrical resistance has the PANi. The conductivity was calculated by using the following equation:

$$\sigma = (\Delta I^* d)/(\Delta U^* A),$$

where $\sigma$ is the conductivity (S cm^{-1}), $\Delta U$ is the potential difference (V), $\Delta I$ is the responsive current difference (A), $d$ is the thickness of the sample (cm) and $A$ is the area (cm^{2}).

The data given in table 1 and figure 5 obtained from the CV diagrams show that the conductivity of the sawdust–PANi composites depends nonlinearly on the aniline:sawdust ratio. We chose the sample with the ratio of 1:2, which had conductivity in the middle of the curve (65.2 mS cm^{-1}), for the study of Cr(VI)’s adsorption ability.
Figure 3. IR-spectrum of sawdust–PANi composite (aniline : sawdust ratio is equal to 0.5).

Table 1. Conductivity of sawdust-PANi composites prepared with different aniline : sawdust ratios.

| Aniline:sawdust ratio | conductivity (mS cm$^{-1}$) |
|-----------------------|-----------------------------|
| 1/3                   | 36.5                        |
| 3/8                   | 52.6                        |
| 1/2                   | 65.2                        |
| 3/5                   | 75.1                        |
| 1/1                   | 87.3                        |

3.4. Cr(VI) adsorption on composite

3.4.1. Influence of component ratio of composite. We fabricated composites with aniline:sawdust ratios varying from 1:3 to 1 and investigated the Cr(VI) adsorption by these composites as well as by sawdust. The results given in table 2 show that the Cr(VI) adsorption degree of sawdust is 4.13 mg g$^{-1}$, while that of the sawdust–PANi composites have values in the interval 17–19 mg g$^{-1}$. This means that PANi plays an important role in the Cr(VI) adsorption process. The Cr(VI) adsorption ability of the composites depends lightly on their component ratios. The mechanism of Cr(VI) adsorption on the composite may be the exchange between the Cl$^−$ and Cr$_2$O$_7^{2−}$ anion.

3.4.2. Influence of adsorption time. The composite with ratio 1 : 2 was chosen for the study of Cr(VI) adsorption. Figure 6 shows that the adsorption degree increased quickly.
Table 3. Adsorption abilities of Cr(VI) in different pH media (\(C_{\text{Cr(VI)}} = 53.5 \text{ mg l}^{-1}\), aniline : sawdust ratio is equal to 1 : 2, adsorption time: 30 min).

| pH  | Adsorption ability (%) | Adsorption degree (mg g\(^{-1}\)) |
|-----|------------------------|-----------------------------------|
| 1   | 88.08                  | 18.85                             |
| 3   | 80.11                  | 17.90                             |
| 7   | 79.24                  | 17.77                             |

for the first few minutes, and reached approximately 90% after about 30 min, and then the increase slows down considerably. The change in solution colour was clearly observed from dark yellow to colourless during the last minutes of adsorption process.

An adsorption degree of 21.4 mg g\(^{-1}\) was found (figure 6). Correspondingly with this value, the remaining quantity of Cr(VI) in solution after 120 min of adsorption was evaluated to be about 1% (figure 6).

3.4.3. Influence of pH. The results given in table 3 show that there is no large difference in the adsorption abilities of the composite in the media with pH equal to 3 and 7 (<1%), but they are higher than that with pH = 1 by almost 8%. In spite of that, the medium with pH = 7 may be the most efficient one for Cr(VI) treatment.

4. Conclusions

The results of our study show that the adsorption ability of Cr(VI) on all studied composites reached a value larger than 80% in the first 30 min. The adsorption speed of Cr(VI) on the composite depends on the adsorption time. The composite with the aniline : sawdust ratio equal to 1 : 2 may be efficiently used for Cr(VI) treatment in the medium with pH = 7.

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