Preparation of orange peel loaded Zn/Al-HT and its adsorption for Cr(VI) in water

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Abstract: The orange peel loaded Zn/Al Hydrotalcite (Zn/Al-HT) was prepared by coprecipitation method. The effects of calcination temperatures, initial concentrations and pH on the adsorption properties of Cr(VI) were investigated, and the results showed that the calcined orange peel loaded Zn/Al-HT at 300℃(Mod2-LDO-300) had best removal rate of Cr(VI), it can be 96%, and the adsorption capacity is 38.5-106.2mg/g in the range of Cr (VI) initial concentration of 20-80mg/L. The Mod2-LDO-300 has a good adsorption effect at pH 2-8. It is a kind of environmental protection and industrial adsorption material.

1. Introduction
Chromium and its compounds are widely used in industrial production, such as tanning agents for leather, wood preservatives, pigments, refractories. Cr(III) is an essential trace element for human body, while Cr(VI) can denature some proteins in blood, cause anemia, nephritis and other diseases. It will do great harm to organisms if the wastewater containing chromium is discharged directly without treatment. Currently, the methods of treating Cr(VI) in wastewater[1] mainly include ion exchange method, oxidation-reduction method, precipitation method, reverse osmosis method, phytoremediation method, biodegradation method and adsorption method. Because of the high cost and the difficulty in treating sludge with chromium, it is difficult to realize industrialization. The adsorption method is cheap and the adsorbents can be reused by desorption[2].

At present, the adsorption materials used for treating Cr(VI) in wastewater mainly include inorganic and organic adsorption materials, such as zeolite[3], layered metal hydroxide[4-5], activated carbon[6-7], low value biomass waste[8-11] and other organic modified materials[12-13]. The adsorption effect of organic adsorbents is mainly achieved by electrostatic interaction and hydrogen bonding. Although inorganic nano materials have high specific surface area, their adsorption capacity is limited by the weak interaction between them[14] and the pH value of the environment which is almost 1-3[15]. Hydrotalcite, as a kind of inorganic adsorption materials, can effectively remove Cr(VI) in water by ion exchange, memory effect and surface adsorption, and it has good adsorption effect between pH 5-10[16-17].

The modified orange peel and Zn/Al hydrotalcite (Zn/Al-HT) used to removing Cr(VI) have been reported for the moment[18,5]. However, there is seldom literature about biomass loaded hydrotalcite as adsorption material.

In this paper, the orange peel loaded Zn/Al hydrotalcite from modified orange peel filtrate with high specific surface area and rich functional groups[19] were prepared by traditional coprecipitation method. The calcined products were prepared also. The adsorption effect of Cr(VI) on different
adsorption conditions was studied. The waste liquid produced by biomass waste and modified biomass is reasonably utilized to realize the recycling of waste liquid, clean and environmental protection.

## 2. Experimental

### 2.1 Materials and reagents

ZnSO₄·7H₂O, K₂Cr₂O₇, NaOH, NaAlO₂, NaCO₃, H₃PO₄, H₂SO₄, HCl, Ethanol, Acetone, Diphenyl carbazide (C₁₃H₁₄N₄O), All chemicals were analytical reagents (AR grade).

### 2.2 Treatment of orange peel

The orange peel was washed with water, dried in 75°C oven, crushed and sieved through 200 mesh. A certain amount of orange peel powder was soaked in 0.25 mol/L NaOH-ethanol (1:1) mixture for 15 h, the filtrate was retained after filtration and recorded as modifier-1. The orange peel was washed to neutral, and dried in 75°C oven to obtain modified orange peel powder, recorded as modifier-2.

### 2.3 Preparation of Orange Peel loaded Zn/Al-HT

Dissolve ZnSO₄·7H₂O in 120 ml distilled water (solution A) and the NaAlO₂, NaOH, Na₂CO₃ are dissolve in another distilled water of the same volume (solution B). The molar ratio of Zn and Al is 2:1. Solution A and B are added dropwise into distilled water containing modifier by peristaltic pump. after dropping, the slurry was carried out at 75°C, pH=9-10 for 1 h, then aged for 8 h at 80°C. The filter cake was washed to neutral and dried at 80°C to obtain the products recorded as Mod1-HT and Mod2-HT. The calcined products (Mod2-LDO-T) were obtained by calcination at 300-800°C. The unmodified Zn/Al-HT and its calcined products were recorded as ZnxAl-HT (x is the molar ratio of Zn to Al), ZnxAl-LDO-T, respectively.

### 2.4 Adsorption of Cr(VI) on Orange Peel loaded Zn/Al-HT

#### 2.4.1 Methods.

20 mL of Cr(VI) solution with a certain mass concentration were added into conical flask. Several minutes shaking in a constant temperature shaker, the modified Zn/Al-HT or calcined products were added into the solution. After a period of time, solutions were filtered by syringe-driven filter with 0.45 um aperture microporous membrane. The content of Cr(VI) in solution was determined by national standard [20].

#### 2.4.2 Adsorption effect. Removal rate (η)

\[ \eta = \frac{C_0 - C_e}{C_0} \times 100\% \]  

Adsorption capacity (Qₑ/mg·g⁻¹)

\[ Q_e = \frac{C_0 - C_e}{m} \times V \]

where \( C_0 \) is the initial concentration of Cr(VI) (mg·L⁻¹); \( C_e \) is the concentration of Cr(VI) at a certain time / equilibrium (mg·L⁻¹); \( m \) is the mass of adsorbent (g); \( V \) is the volume of Cr(VI) (L).

## 3. Results and discussion

### 3.1. Standard working curve of Cr(VI)

As shown in Figure 1, a series of standard solutions were determined according to the national standard GB 7467-87 using UV-vis spectrophotometer at the wavelength of 540nm.

### 3.2. Effect of adsorption materials

At the conditions of initial Cr(VI) concentration of 20 mg/L, initial pH value of 7, adsorption
temperature of 25℃, adsorption for 2 h, the adsorption effect of different adsorption materials on Cr (VI) was investigated, as shown in Figure 2.

![Figure 1 Standard working curve of Cr(VI).](image1)

![Figure 2 Effect of adsorption materials on removal rate of Cr(VI).](image2)

The Cr(VI) removal rate of both adsorbents is shown in Figure 2. The Zn/Al-HT has better adsorption performance when its molar ratio of zinc and aluminum is 2. The untreated orange peel has a certain adsorption effect on Cr(VI) due to its large specific surface area and rich hydroxyl, carboxyl and hydrogen bonds[17]. The Zn/Al-HT modified by modifier 1 and Modifier 2 has a certain adsorption performance for Cr (VI), and the orange peel loaded Zn/Al-HT calcined at 300°C (Mod2-LDO-300) has a good adsorption effect for Cr (VI), and the removal rate can reach 92% without optimizing the adsorption conditions.

3.3. Effect of calcination temperature
Figure 3 shows the calcined products’ adsorption effect on Cr(VI). It was clear that the calcination temperature has a great influence on the adsorption effect: the removal rate of Cr(VI) by Mod2-LDO-300 is nearly 30% higher than its unburned precursor. When the calcination temperature is higher than 500°C, the adsorption of Cr (VI) is greatly reduced.

3.4. Effect of initial pH
As shown in figure 4, the Mod2-LDO-300 has good adsorption effect on Cr (VI) under acidic, neutral and weak alkaline conditions.

![Figure 3 Effect of calcination temperature on removal rate of Cr(VI).](image3)

![Figure 4 Effect of initial pH on removal rate of Cr(VI).](image4)

3.5. Effect of initial concentration
Figure 5 shows the effect of initial concentrations on removal rate and adsorption capacity of Cr(VI).
With the increase of initial concentration, the removal rate of Cr(VI) by Mod2-LDO-300 decreased significantly, while the adsorption capacity increased significantly. After adsorption for 3 h, the adsorption capacity reached 106.2 mg/g.

Figure 5 Effect of initial concentrations on removal rate(5a) and adsorption capacity(5b) of Cr(VI).

4. Conclusion
Orange peel loaded Zn/Al-HT is a kind of environmental protection and efficient adsorption material, its calcined products (Mod2-LDO-300) has excellent adsorption performance for Cr(VI), the removal rate of Cr(VI) reached as high as 96% without selection of adsorption conditions. With initial concentration of Cr(VI) increasing from 20 to 80 mg/L, an adsorption capacity of 38.5-106.2 mg/g was achieved. Moreover, the Mod2-LDO-300 has an excellent adsorption efficiency at pH 2-8.

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References
[1] Maria C. G., (1995) Toxic and mutagenic effects of chromium(VI). Polyhedron, 15: 3667-3689.
[2] Tang, C. C., Chen, H. M., Liu, M. (2015) Advances in adsorption of phosphate in wastewater by ZnAl and MgAl hydrotalcite. Chem. Ind. & Eng. Pro.(China), 34: 245-251.
[3] Ren, G., Yu, Y., Shi, L. (2015) Experimental study on the adsorption of Cr(VI) on modified zeolite by iron and manganese oxides. Chem. Ind. & Eng. Pro.(China), 34: 1159-1164.
[4] Lazaridis, N. K., Pandi, T. A., Matis, K. A. (2004) Chromium(VI) Removal from Aqueous Solutions by Mg-Al-CO3 Hydrotalcite: Sorption-Desorption Kinetic and Equilibrium Studies. Ind. Eng. Chem. Res., 43: 2209-2215.
[5] Yang, C. Y., Song, F. (2013) Highly Selective and Efficient Removal of Cr(VI) and Cu(II) by the Chromotropic Acid-Intercalated Zn-Al Layered Double Hydroxides. Ind. Eng. Chem. Res., 52: 4436-4442.
[6] Fan, W. J. (2018) The Adsorption Property of Magnetic Fe3O4/Active Carbon for Cr(VI) in Electroplating Waste Water. Surf. Tech., 47: 48-54.
[7] Xiao, F. Y., Lui.Y. G. (2017) Adsorption of Cr(VI) ion by ZnO Modified-polyarylonitrile-based activated carbon adsorbent. J. Environ. Eng. (China), 11: 4079-4084.
[8] Zhang, Z. J., Cheng, P. (2017) Preparation of Pig Manure/Straw Composite Carbon and its Adsorption of Cr(VI). Technology of Water Treatment, 13: 67-71.
[9] Bai, R. S., Abraham, T. E. (2002) Studies on Enhancement of Cr(VI) Biosorption by Chemically Modified Biomass of Rhizopus nigricans. Water Res., 36: 1224 -1236.
[10] Luis, S., González, J. (2010) Thermodynamic and Dynamic of Chromium Biosorption by Pectic and Lignocellulosic Biowastes. J. Water Resource and Protection, 2: 888-897.
[11] Xu, M. F., An, Y., Tang, B. (2018) Preparation of Complex Microballoon with Modified Walnut Shell/Alginate and Adsorption Treatment of Complex Microballoonin Cr(VI) from the Wastewater. J. Guizhou University (Natural Science), 835: 120-124.

[12] Priya, B., Roli, P. (2021) Polyacrylonitrile/clay nanofibrous nanocomposites for efficient adsorption of Cr (VI) ions. J. Polym. Res., 28: 7.

[13] Yang, X., Zhou, Y. H., Sun, Z. J. (2020) Synthesis and Cr adsorption of a super-hydrophilic polydopamine-functionalized electrospun polyacrylonitrile. https://doi.org/10.1007/s10311-020-01086-7.

[14] Xu, Y. f., Zhang,J., Qian, G. R. (2010) Effective Cr(VI) Removal from Simulated Groundwater through the Hydrotalcite-Derived Adsorbent. Ind. Eng. Chem. Res., 49: 2752-2758.

[15] Owlad, M., Aroua, M. K., Daud, W. A. W. (2009) Removal of Hexavalent Chromium contaminated Water and Waste water: A Review. Water Air Soil Poll., 200: 59–77.

[16] Alvarez-Ayuso, E., Nugteren, H. (2005) Purification of Chromium(VI) Finishing Waste waters Using Calcined and Uncalcined Mg-Al-CO₃-Hydrotalcite. Water Res., 39: 2535-2542.

[17] Goswamee, R. L., Sengupta, P., Bhattacharyya, K. G. (1998) Adsorption of Cr(VI) in Layered Double Hydroxides. Appl. Clay Sci., 13: 21-34.

[18] Yang, L., Zhao, H. (2013) Optimization of Adsorption Conditions of Acid-Modified Orange Peel for Cr(VI) in Wastewater. Hubei Agricultural Sci., 52: 2508-2510.

[19] Xue, M. X. (2014) Decolorization of Modified Orange Peel for Methylene Blue Wastewater. J. Jinggangshan Univ. (Natural Science), 35: 35-38.

[20] GB/T 7467-87, Determination of Cr(VI) in water by 1,5-Diphenylcarvazide Spectrophotometry[S]. Beijing: Standards Press of China, 1987.