Leaf char: An alternative adsorbent for Cr(III)

Zhenze Li [a],*, Qiang Tang [a], Takeshi Katsumi [a], Xiaowu Tang [b], Toru Inui [a], Shigeyoshi Imaizumi [c]

[a] GSGES, Kyoto University, Kyoto, Japan
[b] Department of Civil Engineering, MOE Key Lab, Zhejiang University, Hangzhou, China
[c] Department of Advanced Interdisciplinary Science, Graduate School of Engineering, Utsunomiya University, Japan

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ABSTRACT

The speciation of Chromium, a well-known human carcinogen, recently turns to be trivalent Cr(III) in waste waters from metal plating industries due to the progress in plating technology. Leaf char was prepared and testified to act as an alternative for Cr(III) adsorption in this study. Various factors were investigated and the optimums were found to be: dosage $= 2.5$ g L^{-1}, adsorption capacity at 69 mg g^{-1}, equilibration duration $>$ 25 min and pH$>$1.88–4.79. The adsorption is sensitive to and will be enhanced at higher temperature at initial Cr(III) concentrations less than 900 mg L^{-1} while the opposite occurred at concentrations more than 900 mg L^{-1}. The changes of enthalpy and entropy during Cr(III) adsorption were predicted at 22.32 to $-$ 11.15 kJ mol^{-1} and 168.25 to 12.18 J mol^{-1} K^{-1}, respectively. The IR spectroscopy revealed the relationship between Cr(III) adsorption and the functional groups of carboxyl, amine and phosphate in the adsorbent while XRD indicated the effect of carbon black.

1. Introduction

Metal pollution has caused serious environmental and public health problems in many places worldwide [1–5]. Pollution was found present in ground, water, sediment and air. Nguyen et al. reported that the To-Lich and Kim-Nguu River in Hanoi City in Vietnam was heavily polluted by heavy metals including Cr which were released from the battery factory located at Van-Dien area [6]. Not only industrial manufactures, but also the human behavior such as transportation could produce heavy metal pollution to the surroundings [2]. Chromium is a well-known human carcinogen and a potential reproductive toxicant and thus attracts increasing concern regarding environmental pollution. Anthropogenic sources are considered to take major responsibility for heavy metal pollution to the environment [1], including emissions from metal industries, electroplating operations, leather tanning industries, and textile manufacturing etc. [7]. Tzou et al. reported that Cr(III) could be oxidized to more mobile and toxic Cr(VI) in soils containing Mn oxide. As the sources of chromium pollution are clear, then efforts should be made to prevent pollution spread from the point source [8].

The speciation of Chromium in waste waters from metal plating industries was mainly hexavalent in the past but turns to be trivalent recently due to the progress in plating technology [9,10]. Li et al. reported a method to apply Cr–P coatings by electrodeposition from trivalent chromium plating bath [9]. Huang et al. successively

deposited Cr–Ni alloy by electroplating using trivalent chromium [10]. Although the trivalent chromium is less toxicant than the hexavalent one, a bit higher concentration of Cr(III) was required to reach a satisfying level in plating qualities [9]. As a result, Cr(III) become a major concern in the waste water from metal plating factories. Traditional treatment method is precipitation by adjusting the solution pHs. This will greatly increase the cost of the treatment and also the salinity of the wastewater. Although some studies utilizing low cost adsorbents (clay, bacteria, sludge, activated carbon etc.) have been reported [11–15], the performances are limited and thus further development in adsorbent type and improvement in adsorption performance remain a stringent problem.

Firmiana Simplex tree is widely distributed in China, Europe, Japan and the USA. Because of its volumetric size and quantity, a mass of leaves fallen in the autumn will give great burdens to the regional sanitary management [16]. It will be interesting to make this garbage into valuable industrial raw materials. With growing concerns about the global climate change, alternative technique is expected to be developed to decrease the potential CO_2 emission. By charring the abundant bioresource, we can improve the stability of these natural organics which are likely to be decomposed biologically [17], prolong their service period, and thus reach the purpose of decreasing the green house gas emissions.

In previous studies, *Firmiana Simplex* leaf has been successfully made into a promising adsorbent for Pb(II) and Mn(II) removal from aqueous solutions [16,18]. However, we still do not know the behavior and mechanism Cr(III) adsorption on the leaf char (LC). In this study, various influence factors including dosage, temperature, equilibration duration and solution pH were carefully examined. The

* Corresponding author. Graduate School of Global Environmental Study, Yoshida Campus, Kyoto University, Sakyo, Kyoto 606-8501, Japan. Tel./fax: +81 75 753 5116.
E-mail address: lazyhero@live.cn (Z. Li).

FT-IR and XRD spectroscopy studies revealed the relevant adsorption mechanisms and confirmed the presence of: 1) carbons black which guarantees the stability of the adsorbent and 2) functional groups i.e. phosphate and amine which provide active adsorption sites for Cr(III).

2. Experimental

2.1. Materials

Naturally fallen leaf which was collected in October, 2008, was oven dried aerobically at 45 °C overnight, pulverized to pass 24 mesh screen with diameters 355 ± 13 μm and then stored in plastic bags [16]. The leaf powder was placed in a sealed oven with temperatures increased from room temperature by 25–30 °C/min, up to 250 °C and further pertained for 3.0 h anaerobically. A 0.5 cm-diameter hole was left open in the oven box in order to release the volatile products. After cooled naturally to the room temperature, the obtained leaf char was collected and stored for further test.

Stock solution of Cr(III) was prepared by dissolving $Cr(NO_3)_3 6H_2O$ (analytical grade) into de-ionized water to the target concentration. To clean conical flasks and centrifuge tubes, they were immersed in 0.01 M HNO_3 solution overnight and then rinsed three times with de-ionized water.

The Cr(III) laden adsorbent was obtained by centrifuging the slurry at 3000 rpm for 5 min after equilibrium adsorption test. The relevant solution parameters include dosage 10 g L^{-1}, initial Cr(III) concentration 600 mg L^{-1}, equilibration duration at 24 h and temperature at 55 °C.

2.2. Methods

2.2.1. Characterization of the sorbent

The specific surface area of the LC was determined by BET N_2 adsorption test in Zhejiang University, China. The FT-IR spectra of the adsorbents (LC and Cr(III) laden LC) were recorded by Nexus-670 (Nicolet, USA) to investigate the contained functional groups. The samples weighed 1.0 g were dried under infrared radiation for 10 min, mixed KBr (analytical grade), ground into fine powder in a carnelian mortar, compressed into a translucent slice supported by a punched paper under 40 MPa and finally exposed to infrared radiation to determine the IR absorption spectroscopy. The XRD spectra of the both sorbents were done by D/MAX-RA apparatus (Rigaku Corporation, Japan) with the assistance of engineers in the university.

2.2.2. Effect of adsorbent dosage

The adsorbent dosage in the aqueous solution was increased from 0.25 to 0.5, 1, 2, 5, 10 and 20 g L^{-1} in this test. The initial Cr(III) concentration (50, 100 and 200 mg L^{-1}) was prepared by diluting the stock solution into the adsorbent slurry in conical flasks. Then the flasks were put into a thermostatic agitator (25 °C) for 24 h at 180 rpm. The mixture was poured to a centrifuge tube and then subject to centrifuge at 3000 rpm for 5 min. The obtained supernated clear water was sampled to determine the equilibrium Cr(III) concentration by Atomic Absorption Spectroscopy (AAS, AAS Meter, General Analysis, China) [19–22]. Blank tests and duplicates were both conducted.

2.2.3. Effect of pH

The sorbent (400 mg) and 40 mL Cr(III) solution (100 mg L^{-1},) were mixed in cleaned conical flask. The pH of the mixture was adjusted by 0.01–0.1 M HNO_3 or NaOH solution until the pH_i was close to the target value ranged from 2.0 ± 0.2 to 10.0 ± 0.2 with an increment of 1.0. The flasks were then placed in an agitator and rotated at 180 rpm, 25 °C for 24 h. The pH of the mixture was measured after equilibration using a glass potentialmeter. The mixture was then centrifuged at 3000 rpm for 5 min in order to

obtain the supernatant of which the Cr(III) concentration was determined by AAS.

2.2.4. Adsorption kinetics

The adsorbent dosage was fixed at 10 g L^{-1} without pH adjustment while the initial solute concentrations of Cr(III) varied from 50, 100 to 200 mg L^{-1}. The reaction temperature was maintained constant at 25 °C. In order to measure the solute concentration at specific times, the test durations were increased from 3 to 6, 9, 12, 15, 20, 40, 60, 120, 180, 240 and 300 min. At the end of each test, the mixture was taken out of the agitator and centrifuged at 3000 rpm for 3 min. The supernatant was sampled and the Cr(III) concentration was determined by AAS. Blank tests and duplicates were both conducted.

2.2.5. Adsorption isotherms at different temperatures and thermodynamics

The sorbent (10 g L^{-1}) was blended with 10 sets of Cr(III) solution with varied initial concentration from 25 to 1000 mg L^{-1} (25, 50, 100, 200, 300, 400, 500, 600, 800 and 1000 mg L^{-1}) at six different temperatures separately from 5 to 55 °C with an increment of 10 °C. All samples were equilibrated for 24 h in an agitator and the equilibrium Cr(III) concentrations were measured by AAS. Control and parallel tests were conducted.

3. Results and discussion

3.1. Characterization of the sorbent

Table 1 shows the surface properties of the prepared adsorbent. The Specific Surface Area (SSA) was determined at 6.26 m² g^{-1}. The micropore and average pore diameter were determined at 14.0 and 20.0 Å, respectively. The total pore volume reached $3.14E-3$ mL g^{-1}. The SSA of this material is not encouraging compared to other reported porous materials such as activated carbons, zeolites, metal hydroxides. However, the adsorption of inorganic toxicant does not depend merely on the pore space or surface areas, which is favored mainly by physisorption. The reaction between the surface active sites and the objective solute could contribute much more adsorption capacity than the physisorption on pore spaces. The following investigations confirmed these speculations as well as the effectiveness of the prepared material.

Fig. 1 shows the IR spectra of the sorbent (a). The characteristic bands of several functional groups could be identified, i.e. carboxyl, P=O, and amine groups etc. Our previous study confirmed the presence of these functional groups. To estimate the existence of functional group (C=O), the characteristic peak of C=O should first be affirmed (1650–1800 cm^{-1}) [16]. There exists a broad band between 1800 and 1630 without any obvious sharp peak. The other fingerprint bands at 1120, 876 and 715 cm^{-1} could be related to C=O groups. Phosphate is effective to fix metal cations by forming precipitates with very low solubility coefficient. The band at 478 cm^{-1} could be linked to the P=O group of phosphate. The bands at 1620, 1450, 1320 cm^{-1} could be assigned to NH group.

The phosphate in the sorbent may be produced from the phosphor contained in leaf cells, i.e. chlorophyll while the NH group comes from the decomposition of nutritional nitrogen component in natural leaf. These functional groups will be destroyed and lost if the treatment

Table 1
BET N_2 adsorption results for leaf char.

Item	SSA	Micropore diameter	Average pore diameter	Total pore volume	Correlation coefficient
Value	6.26 m²/g	14 Å	20.0 Å	$3.14E-03$ cm³/g	0.999