

## Highly Efficient Adsorption of Cr(VI) by Sakura Leaves from Aqueous Solution

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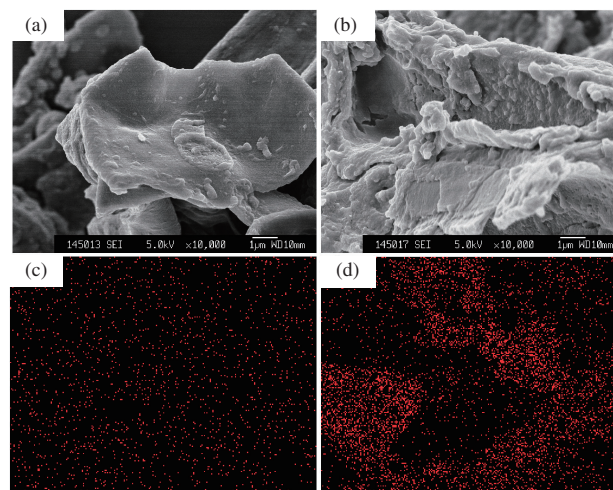
A forestry waste, natural Sakura leaves (SL), was applied to remove Cr(VI) from aqueous solution. SL exhibited a highly effective adsorption performance at optimum pH 1.0. The presence of Cr(III) in equilibrium solution revealed that chemical redox reaction occurred. The results showed that the removal was successfully fitted to the Langmuir model ( $R^2 > 0.99$ ). The theoretical maximum adsorption capacity of Cr(VI) was  $148.12 \text{ mg g}^{-1}$  in static adsorption, which was much higher than similar materials. The study provides a new way to reutilize the SL and indicates a strong potential for waste recycling.

In recent years, ever-increasing use of heavy metals such as Cr, Hg, Cd, and Pd in industrial wastewaters have aroused wide public concern due to their high toxicity and accumulation ability in living bodies. Among them, Cr, widely used in industries of electroplating, steel making, leather tanning, textile dyeing etc., has been considered as a major pollutant. Generally, Cr exists primarily in two valence states: trivalent and hexavalent chromium. Cr(VI) is more toxic than Cr(III) because of its marked carcinogenic, teratogenic, and mutagenic effects on human and other living organisms.<sup>1</sup> Therefore, diverse technologies are largely in need to prevent and remediate Cr(VI) contamination.

Economical, effective, and renewable properties make adsorption remarkable among conventional physical and chemical methods. Forestry and agricultural wastes such as rice straw, walnut shell, coconut shell, etc. used as adsorbents for Cr(VI) removal has been studied by many researchers.<sup>2</sup> Sakura, a world-famous flower, is grown extensively in Japan. As one kind of forestry waste, the amount of autumn Sakura leaves is considerable but they are not effectively utilized except as compost. In the present study, natural Sakura leaves (SL) were prepared and used to remove Cr(VI) from aqueous solution.

SL was collected from the campus of the University of Tsukuba in October. It was washed several times using distilled water and dried in an oven at  $60^\circ\text{C}$  for 24 h. Then it was ground evenly and sieved until the diameter was less than  $105 \mu\text{m}$ . Batch adsorption experiments were carried out in 50-mL plastic centrifuge tubes in static without shaking.  $1000 \text{ mg L}^{-1}$  stock solution of Cr(VI) was prepared and diluted to the desired level with deionized water. 1 M HCl or NaOH was prepared and used to adjust solution pHs. After adsorption, the samples were filtrated using an RC-membrane (Minisart RC 15) with a pore size of  $0.45 \mu\text{m}$ , and then Cr(VI) and total Cr concentrations in filtrate were determined. Each experiment was repeated at least 3 times, and the average result was reported.

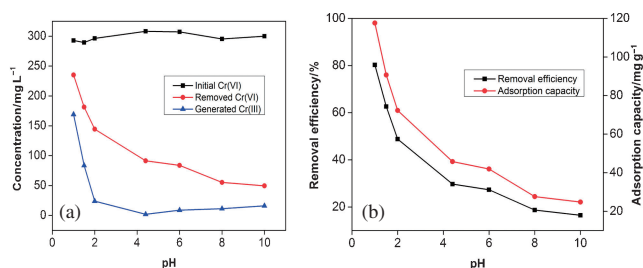
SL and Cr-loaded SL were characterized by energy-dispersive X-ray spectroscopy. Surface and fractured sections



**Figure 1.** Characterization: (a) SEM image of SL, 10000 $\times$ ; (b) SEM image of Cr-loaded SL, 10000 $\times$ ; (c) Cr mapping of SL surface, 1500 $\times$ ; (d) Cr mapping of Cr-loaded SL surface, 1500 $\times$ .

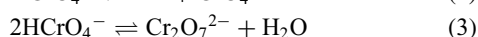
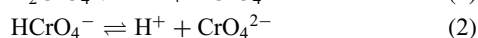
were observed by scanning electron microscope (field emission scanning electron microscope, JSM-6330F, JEOL Ltd., Japan). The images show that SL has a smooth surface with tiny, sparse protuberance (Figure 1a). After Cr(VI) adsorption, the surface became loose, coarse, and disorganized (Figure 1b), indicating the occurrence of violent reactions in the adsorption process. Cr element was not detected before adsorption but clearly observed after adsorption through surface element mapping, as seen in Figure 1c and Figure 1d, indicating that chromium was successfully adsorbed onto the surface of SL.

As is well known, initial pH plays an important role in the Cr(VI) adsorption in aqueous solutions since it affects the surface charge of adsorbents and ionization degree of the adsorbates, which might result in different adsorption process.<sup>3</sup> The effect of pH on Cr(VI) adsorption onto SL was studied in the pH ranges of 1.0–10.0 at ambient temperature. The concentration of the initial Cr(VI) was around  $300 \text{ mg L}^{-1}$  (Figure 2a) and the adsorbent dose was  $2 \text{ g L}^{-1}$ . The removed Cr(VI) and generated Cr(III) in equilibrium solution are shown in Figure 2a, and the removal efficiency and adsorption capacity of Cr(VI) are shown in Figure 2b. It was observed that the maximum removal of Cr(VI) occurred at the pH 1.0. The removal efficiency reached 81% and adsorption capacity was  $117.5 \text{ mg g}^{-1}$  in 24 h. With the increase of pH, the removal efficiency gradually decreased and it declined to less than 20% at pH 10.0. Previous reports have mentioned similar phenomena for the effect of pH on the Cr(VI) removal.<sup>4</sup>



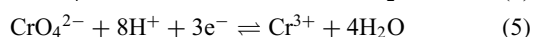
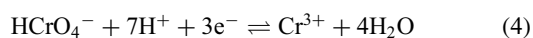
**Figure 2.** Effect of pH on the removed Cr(VI) and the generated Cr(III) (a); effect of pH on the Cr(VI) removal efficiency and the adsorption capacity of the adsorbents (b).

Chromium commonly exists in different oxidation states depending on the pH of the solution system.<sup>1</sup> The transformation equilibrium equations between different valences are as follows:<sup>1</sup>



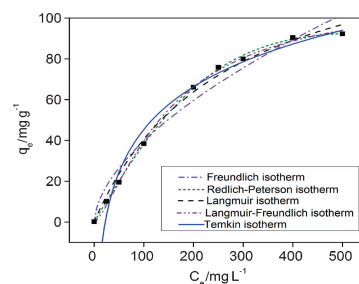
The dominant species of Cr(VI) at low pH is  $\text{HCrO}_4^-$  (usually  $\text{pH} < 6$ ), which gradually changes to  $\text{CrO}_4^{2-}$  with the increase of pH. At a low pH, the surface of SL was positively charged.<sup>5</sup> It is clear that  $\text{HCrO}_4^-$  is more favorable for adsorption due to its lower adsorption free energy and the electrostatic attraction. With the increase of pH, the hydroxyl ions may get attracted to the active opposite polarity charges on the adsorbent surface and the repulsion between the negative-charged surface of adsorbents and the  $\text{CrO}_4^{2-}$  gets stronger which leads to the decline of the adsorption amount.

The amount of Cr(III) in aqueous solution, which was calculated by subtracting the Cr(VI) amount from the total chromium amount, is also shown in Figure 2a. Previous reports have suggested that in acidic solution Cr(VI) stayed in a positive redox condition, which meant that it had a strong oxidizing ability and was unstable in the presence of electron donors. The unsaturated C=C bond and the oxygen-containing functional groups on the surface such as ketone, carboxy, and hydroxy could provide free electrons,<sup>6</sup> bringing about the reduction of Cr(VI) to Cr(III). Cr(VI) oxyanion was transformed to Cr(III) according to the following electron-transfer reactions after interacting with SL.<sup>1</sup>



Analysis of the adjoint curve between the initial concentration of Cr(VI) and the adsorbed amount can be used to describe the equilibrium relationship between adsorbent and adsorbate. To investigate the adsorption equilibrium, Cr(VI) solution over a concentration range of 0–500  $\text{mg L}^{-1}$  was tested at pH 1.0 and with the dosage of 2  $\text{g L}^{-1}$ . Figure 3 shows that the total adsorption amounts and the unit adsorption quantity increase with increasing the initial concentration.

Adsorption isotherms, which applied to data, can indicate the mechanism of the adsorption system. All the nonlinear fitting curves were drawn by the Origin 8.0 software. The curves are presented in Figure 3 and the related parameters, the correlation efficient  $R^2$  and difference degree  $\chi^2$  for each isotherm, are given in Table 1. In general, a higher  $R^2$  and a lower  $\chi^2$  mean a better



**Figure 3.** The various adsorption isotherms of Cr(VI) onto SL.

**Table 1.** The estimated isotherm parameters for Cr(VI) on SL

Isotherms	Equations	Parameters related		Fitting of data	
		Symbol	Estimated value	$R^2$	$\chi^2$
Langmuir	$q = \frac{Q_L K_L C_e}{(1 + K_L C_e)}$	$Q_L$	148.122	0.9918	10.616
Freundlich	$q = K_f C_e^{1/n}$	$K_f$	2.68798	0.9638	26.774
		$n$	1.70968		
Temkin	$q = a + b \ln C_e$	$a$	-93.692	0.9845	19.994
		$b$	30.2011		
Redlich-Peterson	$q = \frac{a C_e}{(1 + b C_e^n)}$	$a$	0.41123	0.9993	0.8921
		$b$	0.00003		
		$n$	1.72277		
Langmuir-Freundlich	$q = \frac{q_m b C_e^{1/n}}{(1 + b C_e^{1/n})}$	$q_m$	112.052	0.9982	2.2523
		$b$	0.00090		
		$n$	0.71802		

**Table 2.** Comparison of Cr(VI) adsorption capacity by similar materials

Materials	Ash /%	Cellulose /%	Hemicellulose /%	Lignin /%	$Q_{\text{max}}$ / $\text{mg g}^{-1}$
Oak chips	1.8	49.7	19.1	5.4	0.47
Almond shells	0.8	29.0	35.2	30.0	3.40
Coconut husk	—	14.0	32.0	46.0	29.0
Rice husk	17.0	35.0	25.0	20.0	52.1
Sakura leaves	11.4	16.6	10.4	18.3	148.12

fitting for the curves. By comparing the two most common isotherms, the Langmuir and the Freundlich, the former fitted the experimental data better with a higher correlation coefficient  $R^2 = 0.9918$ . Langmuir isotherm is applied to homogeneous adsorption processes, where all adsorption sites possess equivalent affinities.<sup>7</sup> Freundlich isotherm is used in multilayer sorptions on heterogeneous surfaces where the adsorption affinities are not balanced.<sup>8</sup> The satisfactory fitting of Langmuir isotherm suggests that chemical adsorption mechanism may be fit for this adsorption process and chromate may be adsorbed in the formation of monolayer coverage on the surface of SL. The estimated maximum adsorption capacity of Cr(VI) onto SL was 148.12  $\text{mg g}^{-1}$ , which was much higher than most similar materials,<sup>2</sup> as shown in Table 2.

As seen in Table 2, the chemical components of SL are cellulose 16.6%, hemicellulose 10.4%, lignin 18.3%, ash 11.4%, and others 43.3%. Lalvani et al.<sup>9</sup> reported that lignin played an important role in the adsorption process by donating an oxygen electron pair to form complexes with chromium ions in solution.

The amount of inert cellulose and hemicellulose was extremely low compared to other materials, which might be a favorable factor for chromium adsorption. It was worth mentioning that some other unconfirmed chemical components (43.3%) were much more abundant than other similar materials. It was speculated that they were possibly a certain amount of dissolved materials like crude protein,<sup>10</sup> contributing to the Cr(VI) adsorption. To prove the estimation, the oxidation–reduction potential (ORP) of SL-soaked solution at pH 1 for 24 h was investigated. The result showed that the ORP of the blank solution (pH 1) and SL-soaked solution were 479.8 and 403.2 mV, respectively. It demonstrated that there actually was some soluble reducibility substance, which might play an important role in the reduction reaction on the Cr(VI) resulting in the better adsorption capacities.

To sum up, natural SL was proved a highly effective material for Cr(VI) removal from aqueous solution. The adsorption process in the present study provides a new way to reuse wastes and it is meaningful to the resource recycling and environmental protection.

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