# Accepted Manuscript

Title: Adsorption behavior and mechanism of Cr(VI) using Sakura waste from aqueous solution

Author: Wenfang Qi Yingxin Zhao Xinyi Zheng Min Ji Zhenya Zhang

Please cite this article as: W. Qi, Y. Zhao, X. Zheng, M. Ji, Z. Zhang, Adsorption behavior and mechanism of Cr(VI) using Sakura waste from aqueous solution, *Applied Surface Science* (2015), http://dx.doi.org/10.1016/j.apsusc.2015.10.088

Adsorption behavior and mechanism of Cr(VI) using Sakura waste from aqueous solution

Wenfang Qi[a], Yingxin Zhao[a,b*]yingxinzhao@tju.edu.cn, Xinyi Zheng[a], Min Ji[a,b], Zhenya Zhang[c]

[a] School of Environmental Science and Engineering, Tianjin University, Tianjin, 300072, China
[b] Tianjin Engineering Center of Urban River Eco-Purification Technology, Tianjin, 300072, China
[c] Graduate School of Life and Environmental Sciences, University of Tsukuba, Tsukuba, 3058572, Japan

[*] Corresponding author. Yingxin Zhao; School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, China. fax: +86 22 2740 6057. (Y.Zhao).

Graphical abstract
The main chemical components of Sakura leaves are cellulose 16.6%, hemicellulose 10.4%, lignin 18.3%, ash 11.4%, and others 43.3%. The adsorption capacity of Cr(VI) onto Sakura leaves can achieve 435.25 mg $g^{-1}$, much higher than other similar agroforestry wastes.fx1

Highlights

Sakura leaves were prepared to remove Cr(VI) from aqueous solution.
The maximum adsorption capacity of Cr(VI) reached 435.25 mg $g^{-1}$.
Cr(VI) adsorption fitted pseudo-second-order kinetic model.
Isotherm models indicated Cr(VI) adsorption occurred on a monolayer surface.
The influence order of coexisting ions followed $PO_4^{3-} > SO_4^{2-} > Cl^-$.

Abstract
A forestall waste, Sakura leave, has been studied for the adsorption of Cr(VI) from aqueous solution. The materials before and after adsorption were characterized by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). To investigate the adsorption performance of Sakura waste, batch experiments were conducted under different adsorbent dosage, contact time, initial concentration of Cr(VI), and co-existing ions. Results showed the data fitted pseudo-second-order better than

pseudo-first-order kinetic model. Equilibrium data was analyzed with Langmuir, Freundlich and Redlich-Peterson isotherm models at temperature ranges from 25 °C to 45 °C. The maximum adsorption capacity from the Langmuir model was 435.25 mg g$^{-1}$ at pH 1.0. The presence of Cl$^{-}$, $SO_4^{2-}$ and $PO_4^{3-}$ would lead to an obvious negative effect on Cr(VI) adsorption, and their influence order follows $PO_4^{3-} > SO_4^{2-} > Cl^{-}$. The study developed a new way to reutilize wastes and showed a great potential for resource recycling.

**Keywords:** Hexavalent chromium; Adsorption; Kinetic; Isotherm; Selectivity; Mechanism

Introduction

With the development of society and economy, the continuously increasing of the industrial pollutants in water, air and soil has proved to be a serious environmental issue in recent years. Especially the heavy metals such as Cr, Pb, Cd, Hg etc. in wastewater play a hazard role due to their toxicity and accumulation ability in living body [1]. Because of the corrosion resistance and aesthetic properties [2], chromium, one of the most usual heavy metals, has been widely used in many engineering industries such as electroplating process, steel making, leather tanning, textile dyeing, pigment manufacture, wood preservatives and so on [3,4]. Generally, chromium exists primarily in two valence states, trivalent and hexavalent chromium. The trivalent form is instable and easily oxidized to high valence state in the oxic conditions. However the two forms are not really the same. The Cr(III) in low concentration is considered to be a necessary micro-nutrient for human beings as an important element in insulin metabolism [5,6]. The toxicity of Cr(VI) is about 100 times greater, and the high oxidation potential and the ability to penetrate biological membranes lead to strong carcinogenicity [7]. And Cr(VI) is more mobile in water and often occurs in industrial effluents as highly soluble chromate ($CrO_4^{2-}$), hydrochromate ($HCrO_4^{-}$) or dichromate ($Cr_2O_7^{2-}$) depending on the solution pH [8]. To prevent the harmful impact on human beings, the World Health Organization regulates a maximum contaminant of 0.05 mg L$^{-1}$ for total Cr in drinking water.

Nowadays, numbers of technologies have been introduced to deal with Cr(VI) in water, such as adsorption, chemical precipitation, ion-exchange, nanofiltration and ecological remediation [8–11]. However, these methods always have some unsatisfactory characteristics like low adsorption ability, high cost and difficult recycling. Among these methods, adsorption is considered to be a more effective and simple method for the Cr(VI) removal from the wastewaters.

Many forestall and agricultural wastes, such as sawdust, sugarcane bagasse, wheat bran, wheat straw, corn stoves etc., have proved to be effective adsorbents for the removal of Cr(VI) from wastewater [12,13]. Due to the advantages of low cost or no cost, great availability, and easy operation, agroforestry wastes are regarded as potential and promising adsorbents in wastewater treatment [14]. Sakura, which belongs to Rosaceae plants, is native to the northern temperate zone, the Himalayan region. It has been

cultivated all over the world but most commonly in Japan. The wide range of Sakura planting has brought a large amount of residues every year. There have been no effective remedies to deal with the fallen leaves so far. Previous studies reported some Rosaceae plants as adsorbents. For instance, almond shell held the maximum Cr(VI) adsorption capacity of 22.20 mg g$^{-1}$ [15]. Apple pulps and plum pulps were also proved to be available in Cr(VI) adsorption [1].

The present study aims to explore the potential of Sakura leave used as an effective adsorbent for Cr(VI) removal. The behavior of Cr(VI) adsorption onto Sakura leaves will be studied through investigating the effects of adsorbent dosage, contact time, initial concentration, and coexisting ions. The adsorption mechanism will be also discussed by combining the data of characterization, kinetics and isotherms.

## Materials and methods
### Materials and chemicals

The Sakura leaves, naturally shriveled and fell down to the ground, were obtained in the campus of the University of Tsukuba, Japan. All the chemicals used in this study are analytical grade. The Cr(VI) stock solution (1000 mg L$^{-1}$) was prepared by dissolving potassium dichromate ($K_2Cr_2O_7$) in deionized water. 1 mol L$^{-1}$ HCl and NaOH were prepared to adjust solution pHs.

### Preparation of adsorbent

The clay and impurities on the surface of the leaves were cleaned up with deionized water after collection. The leaves were then dried up in an oven at 60 °C and grinded to powder which afterwards went through the griddle with pores of 105 micrometer in diameter. Finally the fine particles were kept in an airtight bottle for further use. The main chemical components of Sakura leaves are cellulose 16.6%, hemicellulose 10.4%, lignin 18.3%, ash 11.4%, and others 43.3%.

### Characterization

Several methods have been used to characterize the microstructure and chemical components of the adsorbent. The FTIR technique (FT/IR-300E, Jasco, Japan) was used to study the functional groups which are responsible for Cr(VI) uptake on the surface of the particles. FTIR was recorded at a frequency region of 4000–400 cm$^{-1}$ using KBr pellet at a resolution of 4 cm$^{-1}$. The XPS (PHI-1600, ESCA, USA) was conducted to analyze the elemental composition of the Sakura particles and the oxidation state of Cr adsorbed.

### Batch experiments of Cr(VI) adsorption

All batch experiments were carried out in 50 mL polyethylene glass test tubes in static state. Several experimental parameters which may influence the absorption efficiency were studied, including adsorbent dosage (1 ~10 g L$^{-1}$), contact time (0 ~ 48 h), initial

concentration of Cr(VI) (0 ~ 500 mg L$^{-1}$), temperature (25$^{o}$C ~ 45$^{o}$C), and coexisting ions (Cl$^{-}$, SO$_4^{2-}$, PO$_4^{3-}$). In our previous study, it was found that the optimum adsorption condition occurred at pH 1.0 [16]. Thus, the initial pH of the adsorbate solutions was adjusted to 1.0 and the pH was measured with a pH meter. After finishing each experiment, the suspensions went through the 0.45 μm filter membrane to separate the adsorbent from solution. The concentration of Cr(VI) in solution was analyzed by 1,5-diphenylcarbazide colorimetric method with a UV-vis spectrophotometer at 540 nm wavelength. The concentration of Cr(III) was determined from the difference of the concentration between the total and hexavalent chromium. All the experiments were carried out three times and average values were taken as the calculating data. The adsorption capacity (q) of Cr(VI) was defined as the mass of substrate bound on a gram of adsorbent. The adsorption capacity (q) and removal percentage (R %) of Cr(VI) are calculated by the following equation:

$$(1)\, q = \frac{(c_0 - c_e) \times V}{W}$$

$$(2)\, R(\%) = \frac{c_0 - c_e}{c_0} \times 100$$

where C$_0$ (mg L$^{-1}$) represents the initial concentration and the C$_e$ (mg/L) is the final adsorption equilibrium concentration. W is the mass of adsorbent used (g), and V is the volume of solution (L).

Results and discussion
Effect of the amount of the adsorbent

Adsorbent dosage is considered to be a significant parameter in the removal of Cr(VI) in aqueous solution, since it could change the adsorbent-adsorbate equilibrium of the system [17]. To determine the appropriate adsorption condition, the experiment was carried out with the Cr(VI) concentration of 300 mg L$^{-1}$ at optimal pH 1.0 in 24 hours. The adsorption capacity and the removal efficiency are illustrated in Fig. 1 Fig. 1 It shows that with the increase of the adsorbent dosage, the removal efficiency increases continuously because of the more availability of binding sites for the heavy metal [16]. When the adsorbent dosage takes 4 g L$^{-1}$, the efficiency can almost reach 100%. However, the adsorption capacity decreases resulting from the competition among the large number of the adsorbing surface of the adsorbent [18]. Thus choosing a rational adsorbent concentration in the sewage treatment with a comprehensive consideration is necessary. In this study, the adsorbent dosage was selected as 2.0 g L$^{-1}$ for further experiments.

Effect of contact time and adsorption kinetics

The contact time between the adsorbate and the adsorbent is also an important parameter which is worthy of consideration in the wastewater treatment. To investigate the effect of

contact time on Cr(VI) and total Cr, the experiment was conducted with the initial Cr(VI) concentration of 300 mg L$^{-1}$ and the initial pH of 1.0 without shaking. Fig. 2 Fig. 2 shows the removal efficiency of Cr(VI) and total Cr changed with the increasing time. The removal efficiency of Cr(VI) improved rapidly within the first two hours, and approximately 80% Cr(VI) was removed. In the next 48 hours, the adsorption was still going on with a much slower speed and at last it could reach the removal efficiency of 92.8%. The difference in the removal efficiency between Cr(VI) and total Cr stated that about 60% of Cr(VI) was transformed to Cr(III) in the experiment.

To test the adsorption kinetics in this experiment, the Lagergren-first-order kinetic [19] and pseudo-second-order kinetic [20,21] were expressed in forms:

$$(3)\ \text{Lagergren-first-order} : q_t = q_e \left(1 - e^{-k_1 t}\right)$$

$$(4)\ \text{Pseudo-second-order} : q_t = \frac{k_2 q^2 e^t}{1 + k_2 q e^t}$$

where $q_e$ and $q_t$ (mg g$^{-1}$) are the amounts of removed Cr(VI) at equilibrium and at time t, respectively. $k_1$ and $k_2$ are the adsorption rate constants of pseudo-first-order and second-order models.

Kinetic parameters were calculated and shown in Table 1 Table 1. Fig. 3 Fig. 3 showed this adsorption process was fitted the Pseudo-second-order kinetics better with a higher correlation ($R^2 = 0.9978$) and lower degree of difference ($\chi^2 = 4.2277$). It indicated that the rate-controlling step was chemical adsorption in the process. Similarly several researchers had tested pseudo-second-order kinetic model on different adsorbing materials which also got favorable match [22–26].

Effect of the initial concentration of Cr(VI) and adsorption isotherms

The experiment was taken at 35 °C and 45 °C in the comparison with the previous result at 25 °C [16]. The amount of adsorbed Cr(VI) related with the initial concentration and temperature was evaluated using three common models including the Langmuir, Freundlich and Redlich-Peterson adsorption isotherm [16].

Table 2 Table 2 showed the related parameters and the correlation efficient $R^2$. The value of the parameters was calculated from a non-linear plot. It was observed that there was an increase in the uptake of Cr(VI) with the increase of temperature which might result from an increasing thermal energy of the adsorbing species. The Redlich-Peterson isotherm with three parameters showed better fitting to the curves than the two-parameters isotherms. It was mainly because the Redlich-Peterson isotherm combined all the influence factors from both the Langmuir and Freundlich isotherm leading to its wide application in both homogeneous and heterogeneous systems. Compared the two most

common models used, the Langmuir isotherm gave a better relativity. It indicated chromium ions might be adsorbed in the formation of monolayer coverage on the surface of the adsorbents [27].

Selective evaluation

Generally, industrial water is a complicated system where the appearance of Cr(VI) always accompanies lots of co-existing ions with high ionic strength [28]. As these may affect the adsorption process and influence the application of adsorption materials in the wastewater treatment to some extent, the selective is thought to be an important factor for the adsorbents. The negative effects may produce in two ways: competing in adsorption or acting as counter ions. The adsorption affinity is represented in term of the distribution coefficient, $K_d$ (mL $g^{-1}$), which can be written as [28]:

$$(7)\ K_d = \frac{(c_0 - c_e)}{c_e} \times \frac{V}{W}$$

Where $C_0$ and $C_e$ are the initial and equilibrium concentration of Cr(VI) in the solution, V is the volume of solution (mL) and W is the mass of adsorbent (g). A higher $K_d$ means a stronger chemical binding affinity.

The Cr(VI) adsorption with the presence of $Cl^-$, $SO_4^{2-}$ and $PO_4^{3-}$ which have different elementary composition and chemical valence were tested with initial Cr(VI) concentration of 50 mg $L^{-1}$ and 300 mg $L^{-1}$ while the concentration of co-existing ions were set from $10^{-3}$ mol $L^{-1}$ to $10^{-1}$ mol $L^{-1}$. The $K_d$ values of Cr(VI) in the presence of the three ions were shown in Fig. 4 Fig. 4. Fig. 4a shows that when the initial concentration is 50 mg $L^{-1}$ and the coexisting ions are $10^{-3}$ mol $L^{-1}$, the $K_d$ value reaches over $3.8 \times 10^4$ under a non-coexisting ions systems and it decreases largely to $1.6 \times 10^4$, $1.6 \times 10^4$, $1.2 \times 10^4$ in the presence of $Cl^-$, $SO_4^{2-}$ and $PO_4^{3-}$, respectively.

When the initial concentration became 300 mg $L^{-1}$, the variation trend was similar but its amplitude became smaller. Fig. 4b showed a consistent result with a higher amount of coexisting anions of $10^{-1}$ mol $L^{-1}$. This indicated that the Cr(VI) can be affected by the coexisting ions, especially in a low initial concentration. Compared with Fig. 4a, it is clear that the $K_d$ value decreased in the presence of larger amounts of $Cl^-$, $SO_4^{2-}$ and $PO_4^{3-}$. The observation suggested that the higher ion strengths lead to a larger negative effect on Cr(VI) adsorption.

As shown in Fig. 4, the effect is not only decided by the concentration of initial Cr(VI) and coexisting ions, but also influenced by the chemical valence of anions. The effect follows the order: $PO_4^{3-} > SO_4^{2-} > Cl^-$ which supports the idea that the higher charge density contributes to a stronger competing force for adsorption sites against Cr(VI) ions. Similar observation was obtained by Duranoˇglu et al [29]. Besides, the ionic radius of

$PO_4^{3-}$, $SO_4^{2-}$ and $Cl^-$ are 2.38 Å, 2.30 Å, and 1.81 Å, respectively [30]. It can be speculated that their close order to $HCrO_4^-$ follows $PO_4^{3-}> SO_4^{2-} > Cl^-$. The similar molecular dimensions and hydration energy could compete adsorption sites more intensely against Cr(VI) anions, which might be another possible reason for the influence order.

Adsorption mechanism

The FTIR technology was proved to be a useful tool to determine the functional groups which were responsible for Cr(VI) adsorption on the surface of the adsorbent. The infrared spectra of Sakura before and after Cr(VI) adsorption were shown in Fig. 5 Fig. 5 It can be seen that the absorbance band at 1735 and 3422 cm$^{-1}$ was the O-H stretching vibration, indicating that some hydroxyl groups were formed on the surface of Sakura [31]. The peaks at about 1067, 1629 and 2923 cm$^{-1}$ are usually assigned to -CO, -C=N and –CH groups, respectively. The absorption at around 1312 cm$^{-1}$ means the presence of –CH$_2$ group [32]. For the spectrum after the adsorption of Cr(VI), the new peak at 781 cm$^{-1}$ might be due to the interaction between the adsorbent and Cr(VI).

XPS was utilized to further explain the mechanism of the Cr(VI) adsorption onto Sakura. This technology could not only provide element analysis of carbon, oxygen, chromium and other elements, but also provide valuable information about the change of chemical valence state by examining the shift in binding energy since the binding energy will increase when more electron density gets away from the electron shell [33]. Therefore, the change process of Cr states and main functional groups from unsaturated to saturated adsorption could be well analyzed by XPS.

To define the different situation of unsaturated and saturated adsorption, different adsorbent dosages were selected based on our previous experimental results in Section 3.1. For saturated adsorption, 2 g L$^{-1}$ adsorbent dosage was used and the removal efficiency of Cr (VI) was 92.8% under the condition of initial concentration 300 mg L$^{-1}$ and pH 1 at 25$^{o}$C. For unsaturated adsorption, 10 g L$^{-1}$ adsorbent dosage was added and the removal efficiency of Cr (VI) was 100%. The survey spectra were shown in Figs. 6 and 7 Figs. 6 and 7. Fig. 7a showed the region scan of natural Sakura surface before exposed to the aqueous solution. Fig. 7b and c displayed the changed surfaces of unsaturated and saturated adsorption of Cr(VI). As shown in Fig. 6, it was obvious that carbon and oxygen were predominant elements on Sakura surface. The C 1s spectrum was resolved into three individual peaks: C-C group (284.53eV-284.68 eV), C-O group (284.81eV-285.46 eV) and O=C-O group (286.68eV-287.82 eV) [34]. From the three spectra in Fig. 7a1, b1 and c1, the C-C group showed a notable decrease together with an increase in the C-O group after Cr(VI) adsorption. It indicated that the C-O group was created on the surface by the powerful oxidation of Cr(VI) with a parallel chemical redox reaction taken place to the C-C group. From unsaturated to saturated adsorption,

O═C-O group increased, revealing the further oxidation process of carbon element on Sakura surface.

Detailed XPS survey of the regions for Cr 2p was shown in Fig. 7 a2, b2, and c2. Cr element was detected which indicated the successful adsorption of chromium on the Sakura surface. As shown in Fig. 7, the adsorbed chromium predominantly existed in trivalent form, and only a small amount was present as Cr (VI). From unsaturated to saturated adsorption, the ratio of Cr(VI) decreased from 33.9% to 19.2%, and the ratio of Cr(III) increased from 66.1% to 80.8%.

On the basis of the above analysis, the adsorption mechanism was speculated to have three steps. Firstly, Cr(VI) anions are bounded to the activated groups on the surface of the adsorbent. Secondly, most Cr(VI) anions are reduced to Cr(III) by the redox reaction with the oxidation of C groups. Finally, some of the reduced Cr(III) are released to the aqueous and the rest adsorbed anions are involved in complexation reaction with functional groups [35].

Comparison with other similar materials

The similar adsorbents used for the adsorption of Cr(VI) are summarized in Table 3 Table 3. Comparing to other wastes, Sakura leaves showed a much higher adsorption capacity of 435.25 mg g$^{-1}$ for Cr(VI) removal from aqueous solution. Although the optimal pH 1.0 is highly acidic, it can be exactly suitable to treat Cr(VI) from some industrial effluents such as electroplating wastewater (pH 1.0-2.0) [36], which indicating its promising application in practice.

Conclusion

In this work, the natural Sakura leave was applied to remove Cr(VI) from aqueous solution and it showed an effective performance with high adsorption capacity of 435.25 mg g$^{-1}$. The adsorption ability depended on adsorbent dosage, contact time, initial Cr(VI) concentration and coexisting ions. The Cr(VI) adsorption onto Sakura leave was best explained by the pseudo-second-order kinetic model. Adsorption isotherm models indicated the process was occurred on a monolayer surface. XPS analysis confirmed that Cr(VI) adsorption was accompanied by the redox reaction. The findings in present study proved that Sakura was a cost-effective and efficient adsorbent for Cr(VI) removal.

# References

[1] P. Miretzky, A.F. Cirelli, Cr(VI) and Cr(III) removal from aqueous solution by rawand modified lignocellulosic materials: a review, J. Hazard. Mater. 180 (2010) 1.

[2] M. Baikousi, A.B. Bourlinos, A. Douvalis, T. Bakas, D.F. Anagnostopoulos, J.Tucek, K. Safarova, R. Zboril, M.A. Karakassides, Synthesis and characterization of c-$Fe_2O_3$/carbon hybrids and their application in removal of hexavalent chromium ions from aqueous solutions, Langmuir, 28 (2012) 3918.

[3] Q.X. Zhou, Y.F. Song, Remediation of Contaminated Soils: Principles and Methods, Science Press, Beijing, 2004.

[4] K. Kannan, Fundamentals of Environmental Pollution, S. Chand and Co. New Delhi, 366.

[5] Y. Hou, H. Liu, X. Zhao, J. Qu, J.P. Chen, Combination of electroreduction withbiosorption for enhancement for removal of hexavalent chromium, J.Colloid Interf. Sci. 385 (2012) 147.

[6] D.M. Proctor, M. Suh, S. L.Campleman, C. M.Thompson, Assessment of the mode of action for hexavalent chromium-induced lung cancer following inhalation exposures Review Article, Toxicology 325 (2014) 160.

[7] H. Shen, Y. Wang, Simultaneous chromium reduction and phenol degradation in a coculture of Eschericha coli ATCC 33456 and Pseudomonas putida DMP-1,Appl. Environ. Microbiol. 61 (1995) 2754.

[8] D.Mohan, C.U. Pittman Jr., Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, J. Hazard. Mater. 137 (2006) 762.

[9] X. Zhou, T. Korenaga, T. Takahashi, T. Moriwake, S. Shinoda, A process monitoring/controlling system for the treatment of wastewater containing chromium(VI), Water Res. 27 (1993) 1049.

[10] S.A. Cavaco, S. Fernandes, C.M. Augusto, M.J. Quina, L.M. Gando-Ferreira, Eval-uation of chelating ion-exchange resins for separating Cr(III) from industrialeffluents, J. Hazard. Mater. 169 (2009) 516.

[11] Y.X. Liu, D.X. Yuan, J.M. Yan, Q.L. Li, T. Ouyang, Electrochemical removalof chromium from aqueous solutions using electrodes of stainless steel netscoated with single wall carbon nanotubes, J. Hazard. Mater. 186 (2011) 473.

[12] D.C. Sharma, C.F. Forster, A preliminary examination into the adsorption of hexavalent chromium using low-cost adsorbents, Bioresour. Technol. 47 (1994) 257.

[13] L. Dupont, E. Guillon, Removal of hexavalent chromium with a lignocellulosic substrate extracted from wheat bran, Environ. Sci. Technol. 37 (2003) 4235.

[14] L.H. Wartelle, W.E. Marshall, Chromate ion adsorption by agricultural by-products modified with dimethyloldihydroxyethylene urea and choline chloride, Water Res. 13 (2005) 2869.

[15] X.S. Wang, L.F. Chen, F.Y. Li, Removal of Cr(VI)with wheat-residue derived black carbon: reaction mechanism and adsorption performance, J.Hazard. Mater.175 (2010) 816☐

[16] W.F. Qi, Y. Wang, M. Ji, Y.X. Zhao, Highly efficient adsorption of Cr(VI) by Sakura leaves from aqueous solution, Chem. Lett. 44 (2014) 697.

[17] H. Deveci, Y. Kar, X. Wang, J. Li, Adsorption of hexavalent chromium from aqueous solutions by bio-chars obtained during biomass pyrolysis, J. Ind. Eng. Chem. 19 (2013) 190.

[18] Z. Wang, C. Ye, Adsorption and desorption characteristics of imidazole-modified silica for chromium(VI), Appl. Surf. Sci. 287 (2013) 232.

[19] S. Lagergren, About the theory of so-called adsorption of soluble substances, Kungliga Svenska Vetenskapsakademiens, Handlingar 24 (1898) 1.

[20] Y.S. Ho, G. Mckay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water Res. 34 (2000) 735.

[21] S. Azizian, Kinetic models of sorption: a theoretical analysis, J. Colloid Interf. Sci. 276 (2004) 47.

[22] Y. Zhou, Q. Jin, T. Zhu, Y. Akama, Adsorption of chromium(VI) from aqueous solutions by cellulose modified with β-CD and quaternary ammonium groups, J. Hazard. Mater. 187 (2011) 303

[23] F. Granados-Correa, J. Jiménez-Becerril, Chromium(VI) adsorption on boehmite, J. Hazard. Mater. 162 (2009) 1178

[24] X.L. Yang, Q. Jiang, H.L.Song, Selection and application of agricultural wastes as solid carbon sources and biofilm carriers in MBR, J. Hazard. Mater. 283 (2015) 186.

[25] L.A. Rodrigues, L.J. Maschio, F.E. Silva, Adsorption of Cr(VI) from aqueous solution by hydrous zirconium oxide, J. Hazard. Mater. 173 (2010) 630.

[26] M. Bhaumik, A. Maity, V.V. Srinivasu, Enhanced removal of Cr(VI) from aqueous solution using polypyrrole/Fe$_3$O$_4$ magnetic nanocomposite, J. Hazard. Mater. 190 (2011) 381.

[27] K.Y. Foo, B.H. Hameed Insights into the modeling of adsorption isotherm, Chem. Eng. J. 156 (2010) 2.

[28] T. Sangvanich, V. Sukwarotwat, R.J. Wiacek, R.M. Grudzien, G.E. Fryxell, R.S.Addleman, C. Timchalk, W. Yantasee, Selective capture of cesium and thallium from natural waters and simulated wastes with copper ferrocyanide functionalized mesoporous silica, J. Hazard Mater. 182 (2010) 225.

[29] D. Duranoğlu, A.W. Trochimczuk, U. Beker, Kinetics and thermodynamics of hexavalent chromium adsorption onto activated carbon derived from acrylonitrile-divinylbenzene copolymer, Chem. Eng. J.187 (2012) 193.

[30] Yitzhk Marcus, Ions Properties, CRC Press, Har/Dskt edition, 1997.

[31] L. Tang, G.D Yang, Synergistic effect of iron doped ordered mesoporous carbon on adsorption-coupled reduction of hexavalent chromium and the relative mechanism study, Chem. Eng. J.239 (2014) 114.

[32] T.S. Anirudhan, J. Nima, P.L. Divya, Adsorption of chromium(VI) from aqueous solutions by glycidylmethacrylate-grafted-densified cellulose with quaternary ammonium groups, Appl. Surf. Sci. 279 (2013) 441.

[33] M. Baikousi, A. W. Trochimczuk, Kinetics and thermodynamics of hexavalent chromium adsorption onto activated carbon derived from acrylonitrile-divinylbenzene copolymer, Chem. Eng. J.187 (2012) 193.

[34] L.H. Huang, J. Xue, F. Jin, Study on mechanism and influential factors of the adsorption properties and regeneration of activated carbon fiber felt (ACFF) for Cr(VI) under electrochemical environment, J. Taiwan Inst. Chem. Eng. 45 (2014) 2986.

[35] D. Park, Y.S. Yun, J.H. Jo, J.M. Park, Mechanism of hexavalent chromium removal by dead fungal biomass of Aspergillus niger, Water Res. 39 (2005) 533.

[36] D. Chauhan, M . Jaiswal , N. Sankararamakrishnan, Removal of cadmium and hexavalent chromium from electroplating waste water using thiocarbamoyl chitosan□Carbohyd. Polym. 88 (2012) 670.

[37] G.S. Agarwal, H.K. Bhuptawat, S. Chaudhari , Biosorption of aqueous chromium(VI) by Tamarindus indica seeds, Bioresour. Technol. 97 (2006) 949.

[38] S. Arris, M .B. Lehocine , A.H. Meniai., Sorption study of chromium sorption from wastewater using cereal by-products□Int. J. Hydrogen Energ.147 (2014) 1.

[39] S. Rangabhashiyam, N.Selvaraju , Evaluation of the biosorption potential of a novel Caryota urens inflorescence waste biomass for the removal of hexavalent chromium from aqueous solutions, J. Taiwan Inst. Chem. Eng. 47(2015) 59.

[40] T. Altun, E.Pehivan, Removal of Cr(VI) from aqueous solutions by modified walnut shells, Food Chem. 132 (2012) 693.

[41] M. Aoyama, Removal of Cr(VI) from aqueous solution by London plane leaves□J. Chem. Technol. Biotechnol. 78 (2003) 601.

Fig. 1 The effect of adsorbent dosage on the uptake of Cr(VI).

Fig. 2 Effect of contact time on Cr(VI) and total Cr adsorption.

Fig. 3 Adsorption kinetics of Cr(VI) adsorption.

Fig. 4 Variation of the distribution coefficients (concentration of coexisting ion▒=▒10-3 mol L-1 (a) and 10-1mol L-1 (b)).

Fig. 5 FTIR spectra of Sakura before (a) and after (b) adsorption.

Fig. 6 XPS wide scans of the Sakura before adsorption (a); unsaturated (b) and saturated (c) adsorption of in aqueous solution.

Fig. 7 Detailed XPS survey of the region for C 1s and Cr 2p.

Table 1 Kinetic parameters for Cr(VI) adsorption.

| Models | Parameters related | | Fitting of data |
|---|---|---|---|
| | Symbol | Estimated value | $R^2$ |
| Lagergren-first-order | k1 | 0.0308 | 0.9805 |
| | qe | 125.51 | |
| Pseudo-second-order | k2 | 0.0004 | 0.9978 |
| | qe | 131.74 | |

Table 2 The Langmuir, Freundlich and Redlich-Peterson constants for Cr(VI) adsorption.

| Temp. (oC) | Langmuir | | | Freundlich | | | Redlich-Peterson | |
|---|---|---|---|---|---|---|---|---|
| | QL | KL | R2 | Kf | n | R2 | a | b |
| 25 | 148.12 | 0.0038 | 0.9918 | 2.6880 | 1.7097 | 0.9638 | 0.4112 | 3.0000 ×10-5 |
| 35 | 362.87 | 0.0010 | 0.9796 | 1.0925 | 1.3115 | 0.9889 | 0.4779 | 0.0045 |
| 45 | 435.25 | 0.0012 | 0.9992 | 1.3960 | 1.2987 | 0.9977 | 0.5808 | 0.0063 |

Table 3 Comparison with other similar adsorbents for Cr(VI) removal.

| Absorbents | pH optimal | Initial C. (mg L-1) | Dosage (g L-1) | Temperature (oC) |
|---|---|---|---|---|
| Modified Soybean hulls [14] | 3 | 1820 | 10 | 25 |
| T. indica seed [37] | 4 | 50 | 0.5 | 50 |
| Cereal by-products[38] | 6.0 | 132 | 2 | 20 |
| Caryota urens inflorescence [39] | 2.0 | 100 | 1 | 30 |
| Modified walnut shells [40] | 1.0 | 1 | 0.2 | 25 |
| London leaves [41] | 3.0 | 315 | 2 | 40 |
| Sakura leaves | 1.0 | 500 | 2 | 45 |