

Report

Chromium(VI) Adsorption from the Aqueous Phase by Activated Carbon

Fumihiko Ogata,^a Hajime Kimura,^a Chalermpong Saenjum,^{b,c} Takehiro Nakamura,^a and Naohito Kawasaki^{*a,d}

^aFaculty of Pharmacy, Kindai University, 3-4-1 Kowakae, Higashi-Osaka, Osaka 577-8502, Japan; ^bFaculty of Pharmacy, Chiang Mai University, Suthep Road, Muang District, Chiang Mai, 50200, Thailand; ^cCluster of Excellence on Biodiversity-based Economics and Society (B.BES-CMU), Chiang Mai University, Suthep Road, Muang District, Chiang Mai, 50200, Thailand; ^dAntiaging Center, Kindai University, 3-4-1 Kowakae, Higashi-Osaka, Osaka 577-8502, Japan

Received September 14, 2020; Accepted October 16, 2020

The performance of hexavalent chromium (Cr(VI)) adsorption by activated carbon (AC) prepared from coconut shell (AC1) and modified with silver nanoparticles (AC2), titanium oxide (AC3), and magnetic powder (AC4) was evaluated in this study. The interaction between AC surface properties and Cr(VI) was also assessed via elemental distribution and binding energy analyses. More Cr(VI) was adsorbed onto AC1 than onto any other AC, indicating that the specific surface area and surface functional groups are key factors for Cr(VI) adsorption from the aqueous phase (with correlation coefficients of 0.988 and 0.868–0.949, respectively). Activation of the coconut shell with silver nanoparticles, titanium oxide, and magnetic powder did not increase Cr(VI) adsorption. Cr atoms were detected on the AC1 surface by electron probe microanalysis only after adsorption. Moreover, the binding energies of Cr (2s, 2p, 3s, and 3p) and O (1s) were confirmed after adsorption. These results indicate that AC surface properties were strongly related to adsorption performance. Finally, this study reveals the optimal pH conditions for the removal of Cr(VI) from the aqueous phase of approximately pH 2–3 (acidic conditions). In conclusion, this study elucidates the Cr(VI) adsorption mechanisms of coconut shell-derived AC.

Key words activated carbon, chromium(VI) ion, adsorption

INTRODUCTION

In 2015, the United Nations adopted 17 Sustainable Development Goals,¹⁾ including strategies for improving the safety and security of the global water supply. Consequently, water-related environmental problems, such as heavy metal contamination, have become a major concern in recent years. Heavy metals have strong negative effects on the water environment; specifically, hexavalent chromium (Cr(VI)) is one of the most toxic pollutants in terms of its carcinogenic effects and liver toxicity.^{2,3)} Moreover, it is not automatically degraded and exhibits high persistence in aqueous environments. When accumulated at high concentrations, Cr can induce serious issues; it becomes lethal when its concentration reaches 0.1 mg/g body weight.^{4,5)} High exposure to Cr can induce respiratory challenges, skin problems, and cancer.⁶⁾ The effects of Cr exposure on human health, however, depends upon dosage and the particular organ at risk. For example, an acute reaction will only occur above the Cr level LD₅₀ (20–250 mg-Cr(VI)/g body weight).

According to the Agency for Toxic Substances and Disease Registry, Cr(VI) is more toxic to humans and the water environment than Cr(III).⁷⁾ In addition, Cr(VI) compounds are classified as Group 1 (carcinogenic to humans) by the International Agency for Research on Cancer.⁸⁾ The maximum Cr concentration limits in drinking water adopted by the World Health Organization and the United States Environmental Protection Agency are 0.05 ppm and 0.1 ppm, respectively.^{9–11)} Thus, removal of Cr(VI) from the aqueous phase is urgently

required to protect water environments and safeguard human health.

Adsorption treatments for the removal of heavy metals such as Cr(VI) have been widely applied in aqueous environments because of their ease of operation and design, low cost, and high efficiency. Among them, activated carbon (AC) has been widely used for the adsorption of Cr(VI) from water. In recent years, the physicochemical properties of both commercially available AC and AC modified by various materials have been evaluated to determine their Cr(VI) adsorption performance.^{3,7,9,12–14)} These studies focused on adsorption parameters such as initial concentration, pH, temperature, contact time, and solution composition,¹⁵⁾ with some papers evaluating the adsorption mechanism in detail.¹³⁾ The key factors controlling the adsorption of Cr(VI) from the aqueous phase were a higher surface area (higher porosity) and more active functional groups on the AC surface.^{12,16)} However, there are only a few reports on the adsorption mechanism of Cr(VI) by AC, which simultaneously employ elemental distribution and binding energy analyses. Elemental distribution analysis can elucidate the existence of Cr on the adsorbent surface, and binding energy analysis can elucidate the chemical bonding condition. These data are needed to identify the adsorption mechanism of Cr(VI) using AC in detail.

Therefore, this study aims to reveal the relationship between AC surface properties and Cr(VI) adsorption in order to elucidate the detailed mechanism of Cr(VI) adsorption from the aqueous phase by AC. Specifically, the surface properties and adsorption performance are analyzed for different types

*To whom correspondence should be addressed. e-mail: kawasaki@phar.kindai.ac.jp

of AC by simultaneously analyzing the elemental distribution and binding energy.

MATERIALS AND METHODS

Materials Different types of AC (denoted as AC1, AC2, AC3, and AC4) were prepared from materials acquired from Ueda Environmental Solutions Co., Ltd., Osaka, Japan. Briefly, AC1 was produced from high-purity coconut shell, which was modified by the addition of silver nanoparticles (AC2), titanium oxide (AC3), and magnetic powder (AC4), respectively. Moreover, the Cr(VI) ion standard solution ($K_2Cr_2O_4$ in 0.1 mol/L HNO_3), hydrochloric acid, and sodium hydroxide were purchased from FUJIFILMU Wako Pure Chemical Co., Osaka, Japan.

The physicochemical characteristics of AC have been reported in a previous study.¹⁷ Briefly, the specific surface area, pore volume, and surface properties (basic and acidic functional groups, and pH_{pzc}) were measured.^{18,19} In addition, the elemental distribution and binding energy of Cr on the AC surface were measured by a JXA-8530F electron probe micro-analyzer (EPMA; JEOL, Tokyo, Japan) and X-ray photoelectron spectroscopy (XPS; AXIS-NOVA, Shimadzu, Co., Ltd., Kyoto, Japan), respectively, in order to elucidate the adsorption mechanism.

Quantification of Cr(VI) Adsorption A small quantity (0.05 g) of each AC was mixed with a 50-mL Cr(VI) solution of 10 mg/L and 50 mg/L. The reaction solution was subjected to shaking of 100 rpm at 25°C for 24 h. Subsequently, the sample solution was filtered through a 0.45- μ m membrane filter. The concentration of Cr(VI) in the filtrate was measured using inductively coupled plasma optical emission spectrometry (ICP-OES; iCAP 7600 Duo, Thermo Fisher Scientific K.K., Tokyo, Japan). The quantity of adsorbed Cr(VI) was calculated based on the difference in Cr(VI) concentrations before and after adsorption.

Additionally, the effect of pH on Cr(VI) adsorption was demonstrated by mixing the adsorbent (AC1, 0.05 g) with a 50-mL Cr(VI) solution of 50 mg/L at pH 2, 4, 6, 8, and 10, which was adjusted by hydrochloric acid or sodium hydroxide solution. The reaction solution was shaken at 100 rpm at 25°C for 24 h. The quantity of adsorbed Cr(VI) was calculated as described previously. The results in this study are expressed as the mean \pm standard deviation ($n = 2-3$).

RESULTS AND DISCUSSION

AC Surface Properties The physicochemical characteristics of each AC type have been reported in a previous study.¹⁷ Further, scanning electron microscopy (SEM) images revealed a concave-convex surface on AC1 and a large number of small pores on AC2, AC3, and AC4, which were significantly different from AC1 and AC2. These results suggest that the surface characteristics of each AC depended on the treatment process employed for surface activation. Additionally, the values of the specific surface area, pore volume, surface functional groups, and pH_{pzc} for AC1 (978 m^2/g , 0.0350 mL/g, 0.139 mmol/g, and 7.46, respectively) were greater than those for AC2, AC3, and AC4. Therefore, AC surface activation treatments using silver nanoparticles (AC2), titanium oxide (AC3), or magnetic powder (AC4) did not increase the specific surface area, pore volume, surface functional groups, or pH_{pzc} . These results suggest

greater adsorption of heavy metals such as Cr(VI) onto AC1 than onto other types of AC. However, this study only evaluated the performance of AC in the removal of Cr(VI) from the aqueous phase; the mechanism of carbon surface activation with silver nanoparticles, titanium oxide, or magnetic powder was not elucidated in detail. Therefore, further studies are necessary to analyze these activation mechanisms in detail.

Cr(VI) Adsorption Performance The amount of Cr(VI) adsorbed onto the different ACs is shown in Fig. 1. At an initial concentration of 10 mg/L, the amount of Cr(VI) adsorption was equivalent for all ACs except AC4. However, at an initial concentration of 50 mg/L, more Cr(VI) was adsorbed onto AC1 (47.59 mg/g) than onto any other AC (all < 30.3 mg/g; data not shown). Therefore, AC1 was deemed most suitable for the removal of Cr(VI) from aqueous solution in this study. Additionally, the activation of coconut shell with silver nanoparticles (AC2), titanium oxide (AC3), or magnetic powder (AC4) did not increase the adsorption of Cr(VI) from the aqueous phase. Table 1 compares the Cr(VI) adsorption capacity of AC1 with other reported adsorbents. The results reveal that AC1 exhibits the optimum adsorption capability (except compared to PAC-Fe⁰/Ag), indicating that AC1 is suitable for the adsorption of Cr(VI) from the aqueous phase.^{9,13,14,20-22}

The relationship between Cr(VI) adsorption and AC physicochemical properties was assessed to elucidate the adsorption mechanism of Cr(VI) by AC (Table 2). The correlation coefficients between the amount adsorbed and the specific surface area, basic functional groups, and acidic functional groups were 0.988, 0.868, and 0.949, respectively. These results suggest that the AC surface properties are important factors influencing Cr(VI) adsorption from the aqueous phase. In contrast, no relationship was observed between pore volume and the adsorption capability of Cr(VI) in this study. Previous studies reported that pore volumes such as micropores in AC could physically adsorb Cr(VI) from the aqueous phase via Van der Waals forces. Thus, a low pore volume or small pore size would limit interaction with adsorbates in the water phase.^{12,23} Hence, it is likely that the adsorption mechanism of Cr(VI) by AC was more influenced by AC surface properties than internal properties in this study.

Therefore, this study analyzed the interaction between AC surface properties and Cr(VI) to elucidate the adsorption mechanism through elemental distribution and binding energy analyses. First, the elemental distribution of Cr on the AC1

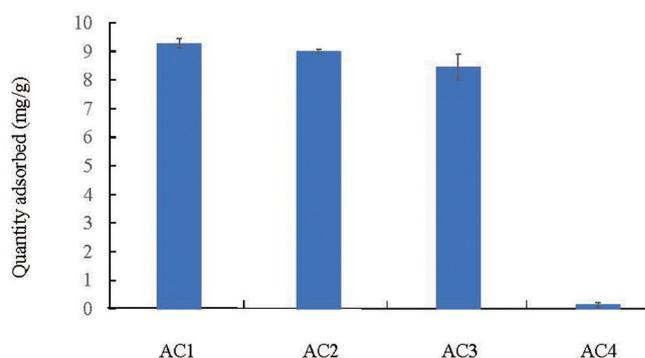


Fig. 1. Amount of Cr(VI) Adsorbed onto ACs

Initial concentration: 10 mg/L, solvent volume: 50 mL, adsorbent: 0.05 g, contact time: 24 h, temperature: 25°C, agitation speed: 100 rpm.

Table 1. Comparison of Cr(VI) Adsorption Capacity of AC1 with Other Reported Adsorbents

Samples	Adsorption capability (mg/g)	pH	Temperature (°C)	Initial concentration (mg/L)	Contact time (h)	Adsorbent (g/L)	References
AC-Fe	34.39	5.38	20	65	10	1	Sun <i>et al.</i> , 2014
PAC-Fe ⁰ /Ag	100	3.0 ± 0.1	25	100	1	0.3	Kakavandi <i>et al.</i> , 2014
δ-FeOOH-coated-γ-Fe ₂ O ₃	25.83	2.5	25	200	0.5	0.1	Hu <i>et al.</i> , 2007
Coconut shell	10.88	4.0	-	25	3	0.25	Babel <i>et al.</i> , 2004
Longan seed	35.02	3.0	45	100	4	0.1	Yang <i>et al.</i> , 2014
RAC	44.05	2	30	200	6	1	Karthikeyan <i>et al.</i> , 2005
AC1	47.59	3	25	50	24	1	This study

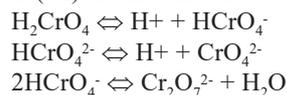
Table 2. Correlation Coefficients of Between Amount Adsorbed and Physicochemical Properties

Samples	Specific surface area (m ² /g)	Pore volume (cc/g)			pH _{pzc}	Basic functional groups (mmol/g)	Acidic functional groups (mmol/g)
		d ≤ 20 (Å)	20 < d ≤ 500 (Å)	500 < d (Å)			
Cr(VI)	0.988	0.752	0.406	0.520	0.583	0.868	0.949

surface before and after adsorption was analyzed (Fig. 2). Cr atoms were only detected after adsorption, indicating that Cr(VI) was present on the AC1 surface after the experiment. Second, the binding energy of Cr on the AC1 surface was analyzed before and after adsorption (Fig. 3). After adsorption, the intensities of Cr (2s, 2p, 3s, and 3p) and O (1s) were determined, confirming the presence of Cr(VI) on the AC1 surface. These results verify that the AC surface properties were crucial for the removal for Cr(VI) from the aqueous phase.

Finally, the effect of pH on Cr(VI) adsorption by AC1 is shown in Fig. 4. The pH in solution is one of the most effective parameters controlling the interaction between Cr(VI) in solution and the AC surface properties. As shown in Fig. 4, adsorption under acidic conditions (approximately pH 2–3) was higher than that under neutral or basic conditions. The AC surface typically exhibits amphoteric properties (positively charged or negatively charged) depending on the solution pH.²⁾ Moreover, ACs contain a large number of surface functional groups (Table 2). Additionally, the different ion species

of Cr(VI) are as follows:²⁴⁾



HCrO₄⁻ is the predominant Cr(VI) species at a solution pH of 2–3; thus, as the pH increased in the experiment, the predominant Cr(VI) species changed from HCrO₄⁻ to CrO₄²⁻ and Cr₂O₇²⁻. Previous studies have reported that HCrO₄⁻ is more favorable for adsorption because it has low adsorption free energy.^{3,25)}

Thus, increasing H⁺ (protons) on the AC surface under acidic pH conditions (approximately 2–3) led to strong electrostatic attraction between the positively charged AC surface and Cr(VI) ion species such as HCrO₄⁻.¹¹⁾ Moreover, as the pH increased, the competition grew between OH⁻ and chromate ions such as CrO₄²⁻ and Cr₂O₇²⁻. In addition, the positively charged surface was significantly weak at increasing the pH (negatively charged when pH > pH_{pzc} in AC1), which indicates the substantial repulsion between AC1 and Cr(VI) in the aque-

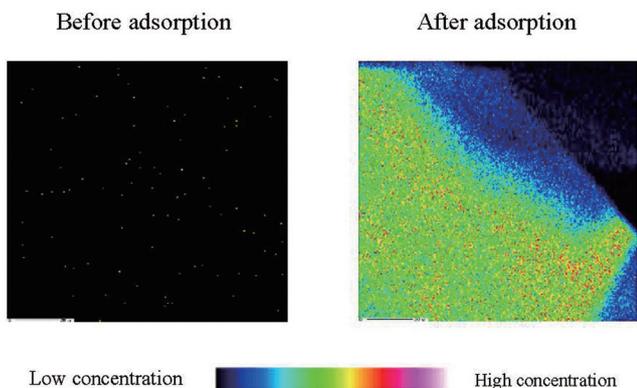


Fig. 2. Elemental Distributions of Chromium onto AC1 Surface before and after Adsorption

Initial concentration: 50 mg/L, solvent volume: 50 mL, adsorbent: 0.05 g, contact time: 24 h, temperature: 25°C, agitation speed: 100 rpm.

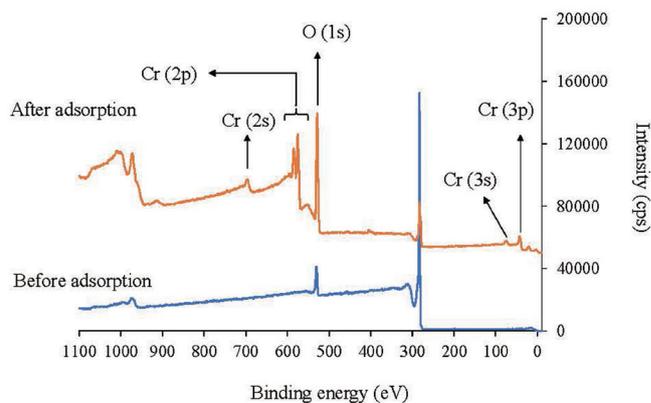


Fig. 3. Binding Energy of Chromium onto AC1 Surface before and after Adsorption

Initial concentration: 50 mg/L, solvent volume: 50 mL, adsorbent: 0.05 g, contact time: 24 h, temperature: 25°C, agitation speed: 100 rpm.

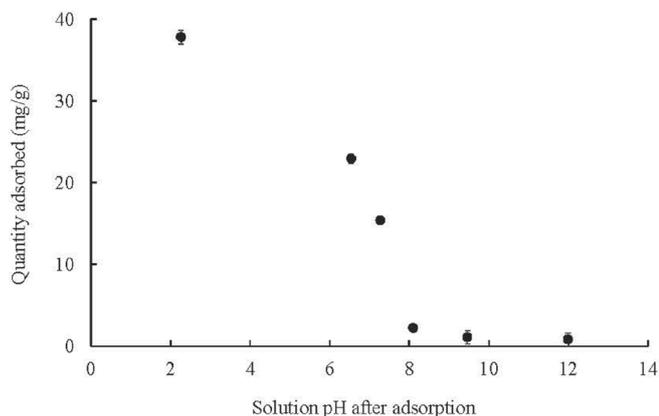


Fig. 4. Effect of pH on the Adsorption of Cr(VI) onto AC1

Initial concentration: 50 mg/L, solvent volume: 50 mL, adsorbent: 0.05 g, pH: 2, 4, 6, 8, 10, and 12, contact time: 24 h, temperature: 25°C, agitation speed: 100 rpm.

ous phase.³⁾ These results also confirm that AC surface properties had a strong influence on Cr(VI) adsorption from the water phase. Furthermore, the optimal pH condition for Cr(VI) adsorption by AC1 was determined as acidic, i.e., approximately 2–3.

In summary, the relationship between AC surface properties and Cr(VI) adsorption was demonstrated in this study. Specifically, the specific surface area and surface functional groups of AC were strongly related to the adsorption of Cr(VI). Additionally, the adsorption mechanisms of Cr(VI) were partially elucidated via elemental distribution and binding energy analyses.

Conflict of interest The authors declare no conflict of interest.

REFERENCES

- United Nations. “About the Sustainable Development Goals” < <https://www.un.org/sustainabledevelopment/sustainable-development-goals/>>, cited 15 April, 2020.
- Cho HH, Wepasnick K, Smith BA, Bangash FK, Fairbrother DH, Ball WP. Sorption of aqueous Zn [II] and Cd [II] by multiwall carbon nanotubes: the relative roles of oxygen-containing functional groups and graphenic carbon. *Langmuir*, **26**, 967–981 (2009).
- Liu W, Zhang J, Zhang C, Wang Y, Li Y. Adsorptive removal of Cr(VI) by Fe-modified activated carbon prepared from *Trapa natans* husk. *Chem. Eng. J.*, **162**, 677–684 (2010).
- AL-Othman ZA, Ali R, Naushad M. Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: adsorption kinetics, equilibrium and thermodynamic studies. *Chem. Eng. J.*, **184**, 238–247 (2012).
- Richard FC, Bourg ACM. Aqueous geochemistry of chromium: a review. *Water Res.*, **25**, 807–816 (1991).
- Achmad RT, Budiawan, Auerkari EI. Effects of chromium on human body. *Annu. Res. Rev. Biol.*, **13**, 1–8 (2017).
- Owlad M, Aroua MK, Wan Daud VMA. Hexavalent chromium adsorption on impregnated palm shell activated carbon with polyethylenimine. *Bioresour. Technol.*, **101**, 5098–5103 (2010).
- World Health Organization (International Agency for Research on Cancer). “Agents Classified by the IARC Monographs, Volumes 1–125” < <https://monographs.iarc.fr/agents-classified-by-the-iarc/>>, cited 15 April, 2020.
- Kakavandi B, Kalantary RR, Farzadkia M, Mahvi AH, Esrafil A, Azari A, Yari AR, Javid AB. Enhanced chromium(VI) removal using activated carbon modified by zero valent iron and silver bimetallic nanoparticles. *J. Environ. Health Sci. Eng.*, **12**, 115 (2014).
- Lv X, Xu J, Jiang G, Xu X. Removal of chromium (VI) from wastewater by nanoscale zero-valent iron particles supported on multiwalled carbon nanotubes. *Chemosphere*, **85**, 1204–1209 (2011).
- Wu L, Liao L, Lv G, Qin F, He Y, Wang X. Micro-electrolysis of Cr (VI) in the nanoscale zero-valent iron loaded activated carbon. *J. Hazard. Mater.*, **254**, 277–283 (2013).
- Zhou J, Wang Y, Wang J, Qiao W, Long D, Ling L. Effective removal of hexavalent chromium from aqueous solutions by adsorption on mesoporous carbon microspheres. *J. Colloid Interface Sci.*, **462**, 200–207 (2016).
- Sun Y, Yue Q, Mao Y, Gao B, Gao Y, Huang L. Enhanced adsorption of chromium onto activated carbon by microwave-assisted H₃PO₄ mixed with Fe/Al/Mn activation. *J. Hazard. Mater.*, **265**, 191–200 (2014).
- Karthikeyan T, Rajgopal S, Miranda LR. Chromium(VI) adsorption from aqueous solution by *Hevea Brasiliensis* sawdust activated carbon. *J. Hazard. Mater.*, **B124**, 192–199 (2005).
- Di Natale F, Lancia A, Molino A, Musmarra D. Removal of chromium ions from aqueous solutions by adsorption on activated carbon and char. *J. Hazard. Mater.*, **145**, 381–390 (2007).
- Chen J, Yiaccomi S, Blaydes TG. Equilibrium and kinetic study of copper adsorption by activated carbon. *Sea Technol.*, **6**, 133–146 (1996).
- Ogata F, Yasuda S, Saenjum C, Nakamura T, Kawasaki N. Interactions of cationic and anionic dyes with activated carbons. *e-J. Surf. Sci. Nanotechnol.*, **18**, 269–274 (2020).
- Boehm HP. Chemical identification of surface groups. *Adv. Catal.*, **16**, 179–274 (1966).
- Pereira MFR, Soares SF, Órfão JJM, Figueiredo JL. Adsorption of dyes on activated carbons: influence of surface chemical groups. *Carbon*, **41**, 811–821 (2003).
- Hu J, Lo I, Chen G. Performance and mechanism of chromate (VI) adsorption by δ -FeOOH-coated maghemite nanoparticles. *Separ. Purif. Tech.*, **58**, 76–82 (2007).
- Kobya M. Removal of Cr(VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: kinetic and equilibrium studies. *Bioresour. Technol.*, **91**, 317–321 (2004).
- Yang J, Yu M, Chen W. Adsorption of hexavalent chromium from aqueous solution by activated carbon prepared from longan seed: kinetics, equilibrium and thermodynamics. *J. Ind. Eng. Chem.*, **21**, 414–422 (2015).
- Rodríguez A, Gracia J, Ovejero G, Mestanza M. Adsorption of anionic and cationic dyes on activated carbon from aqueous solutions: equilibrium and kinetics. *J. Hazard. Mater.*, **172**, 1311–1320 (2009).
- Gurgel LVA, Perin de Melo JC, de Lena JC, Gill LF. Adsorption of chromium(VI) ion from aqueous solution by succinylated mercerized cellulose functionalized with quaternary ammonium groups. *Bioresour. Technol.*, **100**, 3214–3220 (2009).
- Yuan P, Fan M, Yang D, He H, Liu D, Yuan A, Zhu J, Chen T. Montmorillonite-supported magnetite nanoparticles for the removal of hexavalent chromium(VI) from aqueous solutions. *J. Hazard. Mater.*, **166**, 821–829 (2009).