

Article

Efficient Removal of Cr (VI) with Biochar and Parameters Optimized by Response Surface Methodology

Hao Peng *, Jing Guo

Chongqing Key Laboratory of Inorganic Special Functional Materials, College of Chemistry and Chemical Engineering, Yangtze Normal University, Fuling, Chongqing 408100, P. R. China; cqguojing@126.com (J. Guo)

* Correspondence: cqpenghao@126.com (H. Peng)

Abstract: A highly efficient reduction process of Cr (VI) with biochar was conducted in this paper. The results showed that nearly 100% Cr (VI) was reduced at selected reaction conditions: the dosage of biochar at $m(C)/m(Cr) = 3.0$, reaction temperature of 90 °C, reaction time at 60 min and concentration of H₂SO₄ of 20 g/L, respectively. The reduction kinetics analysis demonstrated that the reduction of Cr (VI) fitted well with the pseudo-first-order model and the apparent activation energy was calculated to 40.24 kJ/mol. Response surface methodology confirmed that all the experimental parameters had positive effect on the reduction of Cr (VI). The influence of each parameter on the reduction process followed the order: dosage of biochar > Concentration of H₂SO₄ > Reaction Temperature > Reaction Time. This paper provided a versatile strategy for treatment of wastewater containing Cr (VI) and showed a bright tomorrow for wastewater treatment.

Keywords: Chromium; Response surface methodology; Reduction; Biochar

1. Introduction

Chromium pollution is a serious environmental problem and Cr (VI) has been classified in Group 1 by IARC (International Agency for Research on Cancer) [1-5]. Cr (VI) has many negative impacts on earthworms, plants, fish and so on. It will increase the reproduction and mortality of earthworms, and is toxic on kidney and cells for animals and humans, etc. In recent years, many technologies had been applied to treat the wastewater containing Cr (VI) [6]. The physicochemical technology (like ion exchange, membrane filtrate, chemical precipitation, etc.) were easy to conduct with high removing efficiency [7-10]. The so-called electrochemical technology associated with electricity showed high removal efficiency and being proud of clean and environmental-friendly [11-13]. Photocatalysis and nanotechnology were also developed for treatment of wastewater and showed great performance [14, 15]. While the problems like large scale application, secondary pollution, high cost were remained. Therefore, it is urgent to develop useful technologies for Cr (VI) treatment [16-18]. Recently, reduction of Cr (VI) to Cr (III) had attracted much more attention [12, 13, 19-21].

Biochar derived from plant and animal wastes was a typical adsorbent to remove inorganic and organic pollutants in water due to its low-cost and abundant feed stock availability [22-24]. In addition, the large surface area, high mineral content, and rich oxygen-containing functional groups of biochar were favorable for adsorption of wastewater contaminants such as antibiotics, dyes, and heavy metals [25-27]. Thus, biochar was applied to adsorb chromium (VI) in this paper (actually biochar was acted as a reductant and the adsorption process was proved to be a reduction process). The experimental parameters including the dosage of biochar, reaction temperature, reaction time and concentration of H₂SO₄ on the reduction process were investigated. Also, the reduction kinetics analysis was done.

2. Materials and Methods

2.1 Materials

K₂Cr₂O₇, H₂SO₄ and biochar were of analytical grade and used as received without further purification, which were purchased from Kelong Co., Ltd, Chengdu, China. All solutions were prepared with deionized water with a resistivity greater than 18 MΩ/cm (HMC-WS10) [12, 13, 19, 28].

2.2 Experimental procedure

All the experiments were conducted in a beaker placed in a thermostatic water bath with a temperature precision of ± 0.1 °C [12, 13]. In the batch experiments, 100 mL 1000 mg/L Cr (VI) solution was prepared by dissolving amount of K₂Cr₂O₇ in the deionized water, then the prepared biochar was added into the beaker as the solution was heated to a pre-determined temperature. After a required reaction time, the solution with Cr (III) and retained biochar were separated by vacuum filtration. The concentration of Cr (VI) in the filtrate was determined by ICP-OES [12, 13, 21], and the reduction efficiency (η) of Cr (VI) was calculated following Equation (1):

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

Where, C₀, is the initial concentration of Cr (VI) in the solution, mg/L; C_t, is the concentration of Cr (VI) in the solution at reaction time of t, mg/L.

2.3 Response surface optimization

The interactions between experimental parameters were important for the experimental results while it had been ignored during the single factor experiment, thus, RSM was applied to optimize the experimental process and order the significance of experimental parameters [13, 29, 30]. In this paper, the experimental parameters affected the reduction process were selected as A (m (C)/m(Cr)), B (Reaction Temperature), C (Reaction Time) and D (Concentration of H₂SO₄). The actual values for them were confirmed through the single factor experimental results and displayed in Table 1.

Table 1 Independent variables and factors levels

Independent variable	Unit	Level		
		-1	0	1
A:m(C)/m(Cr)	-	0.5	1.75	3.0
B: Reaction Temperature	°C	30	60	90
C: Reaction Time	min	10	35	60
D: Concentration of H ₂ SO ₄	g/L	0	10	20

3. Results and Discussions

The dosage of biochar had a significant effect on the reduction of Cr (VI) as it was the main reaction reagent. A series of experiments were conducted to investigate the effect of the

dosage of biochar ($m(C)/m(Cr)$) on the reduction efficiency of Cr (VI). The $m(C)/m(Cr)$ was set as $m(C)/m(Cr) = 0.5, 1.0, 1.5, 2.0, 2.5$ and 3.0 , respectively. The other reaction conditions were kept as constant: reaction temperature of $90\text{ }^{\circ}\text{C}$, reaction time of 60 min and concentration of H_2SO_4 at 10 g/L . The results shown in Figure 1a indicated that the reduction efficiency of Cr (VI) was increased with the increasing of $m(C)/m(Cr)$. The reduction efficiency of Cr (VI) was increased from 40.32% to 97.74% as dosage of biochar increased from $m(C)/m(Cr) = 0.5$ to $m(C)/m(Cr) = 3.0$. Thus, the $m(C)/m(Cr) = 3.0$ was selected for further experiments.

Reaction temperature played an important role in a standard chemical reaction. A series of experiments were conducted to investigate the effect of reaction temperature on the reduction efficiency of Cr (VI) and the reaction temperature was set as $30, 45, 60, 75$, and $90\text{ }^{\circ}\text{C}$, respectively. The other reaction conditions were kept as constant: $m(C)/m(Cr) = 3.0$, reaction time of 60 min and concentration of H_2SO_4 at 10 g/L . It could be seen from Figure 1b that the reduction efficiency was increased with the increasing of reaction temperature, and the increasing trend of reduction efficiency was similar with dosage of biochar, which indicated that both dosage of biochar and reaction temperature had significant effect on the reduction process. Higher temperature could intensify the activity of biochar molecule and Cr (VI) ion, promoted the extent of the reduction reaction and enforced the reduction of Cr (VI) [12, 13, 31]. Therefore, $90\text{ }^{\circ}\text{C}$ was selected as the optimal reaction temperature for further experiments.

Recent study indicated that Cr (VI) was easy being reduced to Cr (III) in the strong acidic medium [12, 13, 21]. A series of experiments were conducted at the concentration of H_2SO_4 ranged from 0 g/L to 20 g/L at various dosage of biochar. Figure 1c displayed that the increase of concentration of H_2SO_4 could facilitate the reduction process of Cr (VI). In theoretical, the formation of HCrO_4^- was the main species of Cr (VI) at $0.8 < \text{pH} < 6.8$, and CrO_4^{2-} was the main species at $\text{pH} > 6.8$ (Figure 2a measured by software Visual MINTEQ [32]). Other way, HCrO_4^- was easier reduced into Cr (III) than CrO_4^{2-} as HCrO_4^- the oxidation potential was higher according to the results showed in Figure 2b ($E_0(\text{HCrO}_4^-/\text{Cr}^{3+}) = 1.35\text{ V}$, $E_0(\text{CrO}_4^{2-}/\text{Cr}^{3+}) = 0.56\text{ V}$). When the dosage of biochar was much high, the reduction efficiency had no obvious increase (when $m(C)/m(Cr)$ was up 2.5 , the reduction efficiency of Cr (VI) was nearly 100% at 10 g/L). Thus, concentration of H_2SO_4 at 10 g/L was enough for further experiments.

Figure 1d described the effect of reaction time on the reduction process at various reaction temperatures as other reaction conditions kept as $m(C)/m(Cr) = 3.0$ and concentration of H_2SO_4 at 10 g/L . The results showed that the extend the reaction time could improve the reduction efficiency of Cr (VI) at all reaction temperature. And higher reaction temperature was beneficial for the reduction process, which was consistent with the analysis above.

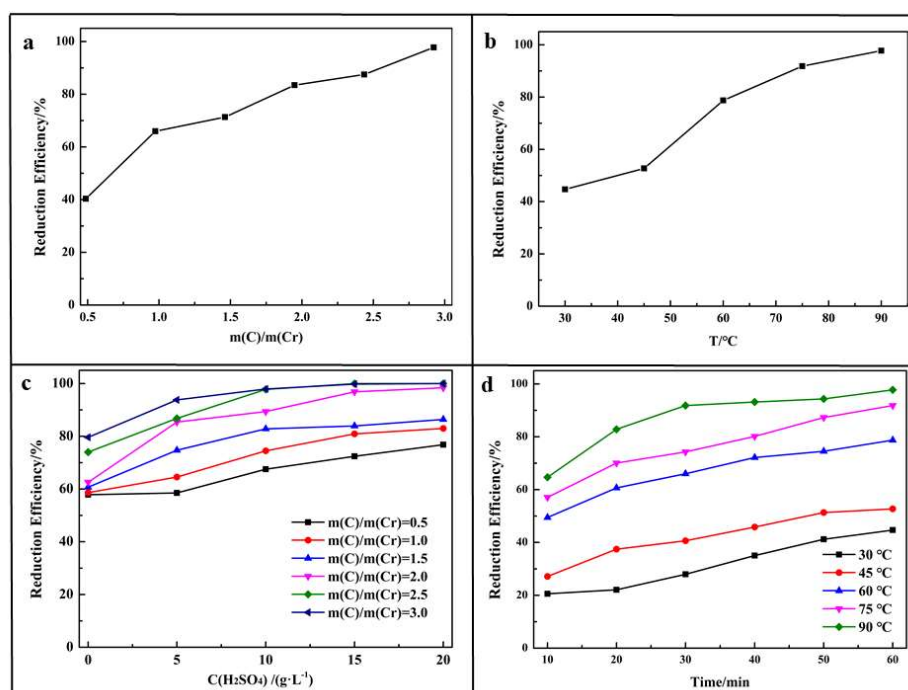


Figure 1 Effect of the single parameters on the reduction process. (a- dosage of biochar (m(C)/m(Cr)); b-Reaction temperature; c-Concentration of H₂SO₄; d- Reaction time)

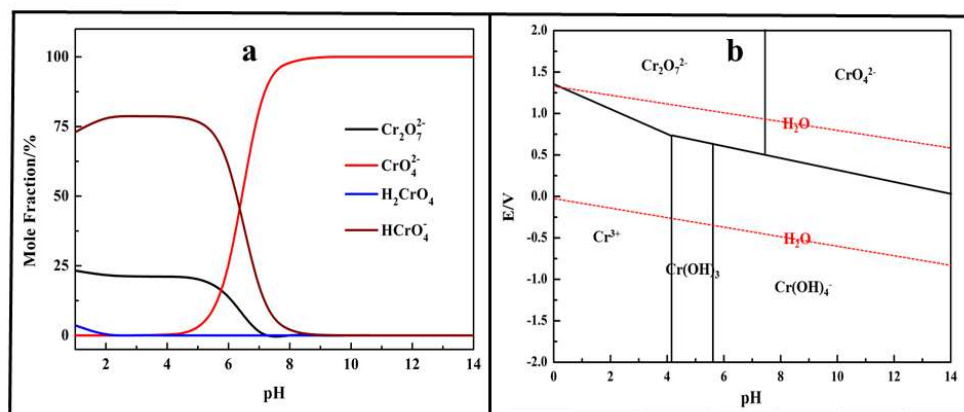


Figure 2 a-Cr(VI) species in the solution at various pH; b-the E-pH diagram of chromium

3.2 Response Surface Methodology

3.2.1 Model fitting

The squares root was used to express the simulated results and it was presented in Equation (2):

$$\sqrt{\eta} = 8.38 + 0.55A + 0.38B + 0.27C + 0.52D - 0.17AB + 0.22AC + 0.25AD - 0.025BC + 0.25BD + 0.20CD - 0.03A^2 + 0.25B^2 + 0.02C^2 - 0.30D^2 \quad (2)$$

The influence of each parameter on the reduction efficiency of Cr (VI) could be seen from the coefficients before them in the Equation (2). The coefficients of them were 0.55, 0.38, 0.27 and 0.52, respectively, which confirmed that all the parameters had a positive effect on the reduction efficiency. The results displayed in Figure 3 indicated that the influence of each parameter on the reduction efficiency followed the order: A > D > B > C, which was consistent with the results described in Equation (2). Above all, the dosage of biochar and concentration of H2SO4 had the greatest influence on the reduction process.

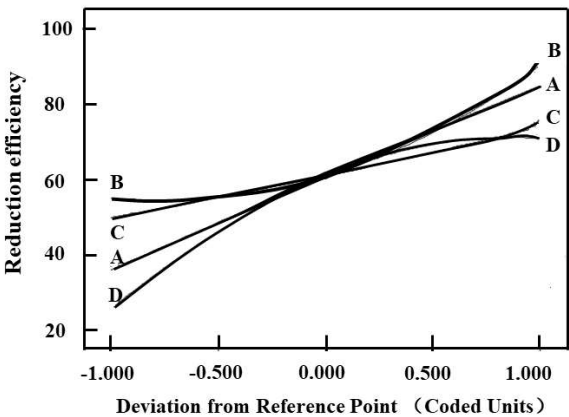


Figure 3 Perturbation plot for the reduction efficiency of Cr (VI) in the design space. (A- (m (C)/m(Cr)); B- (Reaction Temperature); C- (Reaction Time) and D- (Concentration of H2SO4)).

The analysis of variance of the reduction efficiency of Cr (VI) was shown in Table 2. The results showed that the p-value of the model was < 0.0001, which indicated that the selected model was significant and suitable for simulating the reduction process of Cr (VI) [30, 33]

Table 2 Analysis of variance for the response

Source	Sum of Squares	Z	Mean square	F value	p-value Prob>F
Model	11.76	14	0.84	14.47	<0.0001
A	3.60	1	3.60	62.00	<0.0001
B	1.76	1	1.76	30.29	<0.0001
C	0.87	1	0.87	15.05	0.0017
D	3.31	1	3.31	56.94	<0.0001
AB	0.12	1	0.12	2.10	0.1690
AC	0.19	1	0.19	3.36	0.0882
AD	0.24	1	0.24	4.22	0.0591
BC	2.54E-003	1	2.54E-003	0.044	0.8372
BD	0.26	1	0.26	4.39	0.0547

CD	0.16	1	0.16	2.67	0.1243
A ²	5.787E-003	1	5.787E-003	0.100	0.7569
B ²	0.41	1	0.41	7.05	0.0188
C ²	2.533E-003	1	2.533E-003	0.044	0.8375
D ²	0.60	1	0.60	10.32	0.0063
Residual	0.81	14	0.058	-	-
Lack-of-fit	0.81	10	0.081	-	-
Pure error	0.000	4	0.000	-	-

3.2.2 Response surface analysis

To evaluate the fitting effect of the model on the experimental results, some other important diagnostic plots including Internally Studentized Residuals against Run Number, Predicted against Actual, Internally Studentized Residuals against Predicted and Normal Probability against Internally Studentized Residuals, respectively, were shown in Figure 4. All points showed in the Normal Probability against Internally Studentized Residuals plot shown in Figure 4a was concentrated in a straight line illustrated that the error was normally distributed. In a plot of Internally Studentized Residuals against Run Number and Internally Studentized Residuals against Predicted, the residuals were randomly distributed between +3.00 and -3.00, indicating that the Box-Behnken model was successfully established the relationship between the independent variable and the reduction efficiency. A plot of Predicted against Actual was shown in Figure 4b, the points were approximately distributed on a straight line with a slope of 1, which indicated that this model could accurately predict the actual value.

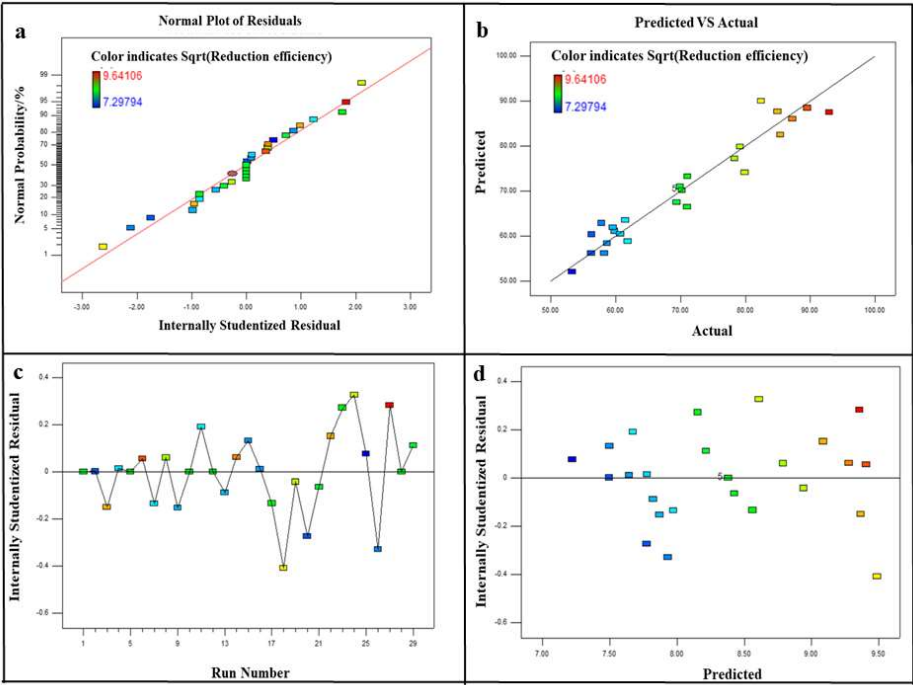


Figure 4 Diagnostic plots of the quadratic model. (a- Normal Probability against Internally Studentized Residuals; b- Predicted against Actual; c-Internally Studentized Residuals against Run Number; d- Internally Studentized Residuals against Predicted)

The contour plots were applied to analysis the interaction between experimental parameters. Figure 5 showed that the reduction efficiency of Cr (VI) was increased with the increase of all experimental parameters and the results were consistent with the analysis above.

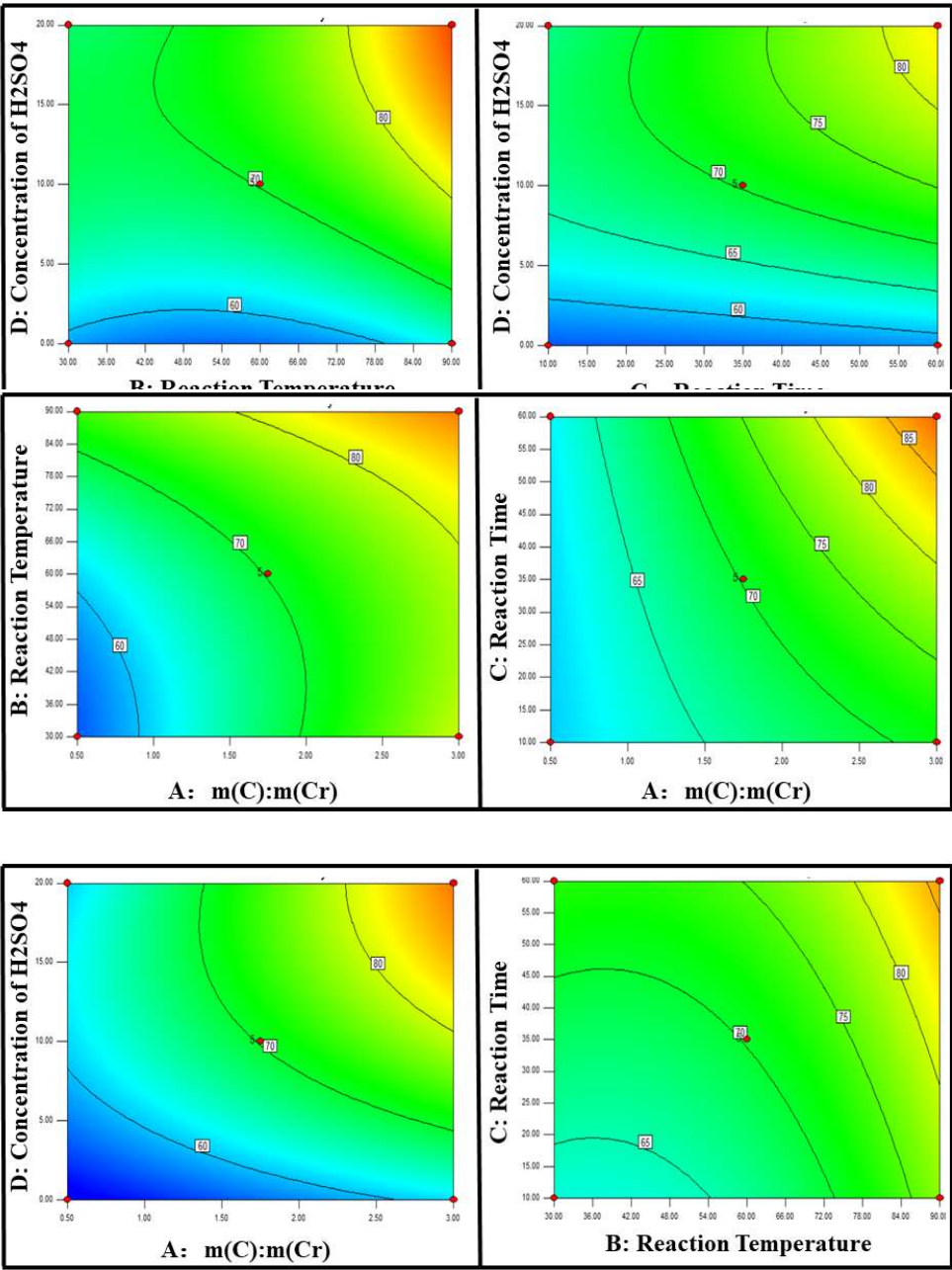


Figure 5 Response surface plots for factors

3.3 Reduction Kinetics Analysis

In this paper, pseudo-first-order model as described as Equation (3) was applied to simulated the reduction behavior of Cr (VI) [33-36].

$$v = dC/dt = -KC \tag{3}$$

Integrate.

$$-LnC = Kt - Ln C_0 \tag{4}$$

Where, v , is the reduction rate of Cr (VI); C , is the concentration of Cr (VI); C_0 , is the initial concentration of Cr (VI); K , is the reduction reaction constant.

Figure 6a displayed the fitting results of experimental results fitted with Equation (4), which indicated that the reduction process of Cr (VI) was fitted well with the pseudo-first-order model. The reduction reaction apparent activation energy was obtained by simulating the experimental results with the Arrhenius Equation (Equation (5)). The apparent activation energy was calculated as 40.24 kJ/mol according to the results showed in Figure 6b, which was much larger than the apparent energy calculated for reduction with oxalic acid (22.49 kJ/mol) [21] and electrochemical reduction (4.74 kJ/mol) [12]. It meant that the reduction process with biochar was harder than oxalic acid and electrochemical reduction.

$$\ln K = \ln A - E_a/RT \quad (5)$$

Where, E_a , is the apparent activation energy; A , is the pre-exponential factor; R , is the molar gas constant, 8.314 J/(mol K); K , is the reduction reaction constant at different reaction temperatures.

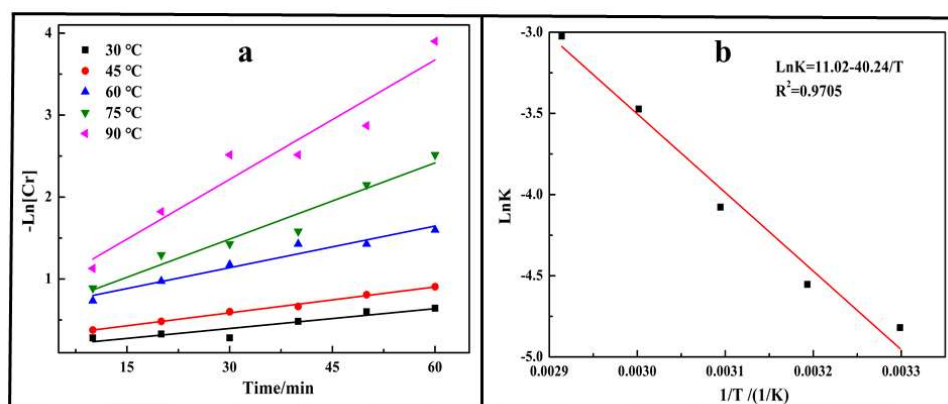


Figure 6 Kinetics plots: a) Plot of reduction kinetics at various reaction temperatures; b) Natural logarithm of reduction reaction constant vs reciprocal reaction temperature

3.4 Removal of Chromium (III)

After the reduction process, the Cr (VI) was reduced to Cr (III) and it was removed by precipitation with sodium hydroxide [37] or adsorption with melamine [19, 20].

4. Conclusions

A highly efficient reduction process of Cr (VI) with biochar was investigated and the following conclusions could be obtained:

- (1) The Cr (VI) was easily being reduced by biochar at high reaction temperature with high dosage of biochar in strong acidic medium. Nearly 100% Cr (VI) was reduced at selected reaction conditions: the dosage of biochar at $m(C)/m(Cr) = 3.0$, reaction temperature of 90 °C, reaction time at 60 min and concentration of H_2SO_4 of 20 g/L, respectively.
- (2) The reduction kinetics analysis indicated that the reduction behavior of Cr (VI) fitted well with the pseudo-first-order model and the apparent activation energy was calculated as 40.24 kJ/mol.

(3) Response surface methodology confirmed that all the experimental parameters had positive effect on the reduction of Cr (VI). The influence of each parameter on the reduction process followed the order: A (dosage of biochar (m (C)/m(Cr)) > D (Concentration of H₂SO₄) > B (Reaction Temperature) > C (Reaction Time). Especially, the dosage of biochar and concentration of H₂SO₄ had the greatest influence on the reduction process.

Author Contributions: Conceptualization, Hao Peng.; methodology, Hao Peng.; software, Hao Peng.; validation, Hao Peng.; formal analysis, Hao Peng.; investigation, Jing Guo; resources, Hao Peng.; data curation, Jing Guo; writing—original draft preparation, Hao Peng.; writing—review and editing, Hao Peng.; visualization, Hao Peng.; supervision, Hao Peng.; project administration, Hao Peng.; funding acquisition, Hao Peng. All authors have read and agreed to the published version of the manuscript.”

Funding: This work was supported by the Science and Technology Research Program of Chongqing Municipal Education Commission (No. KJQN201901403 and No. CXQT20026) and Chongqing Science and Technology Commission (No. cstc2018jcyjAX0018).

Conflicts of Interest: The authors declare no conflict of interest

References

1. J. Song, H. Kong, J. Jang, Adsorption of heavy metal ions from aqueous solution by polyrhodanine-encapsulated magnetic nanoparticles, *J Colloid Interf Sci*, 359 (2011) 505-511.
2. G.Z. Kyzas, K.A. Matis, Nanoadsorbents for pollutants removal: A review, *Journal of Molecular Liquids*, 203 (2015) 159-168.
3. V. Nogueira, I. Lopes, T. Rocha-Santos, F. Gonçalves, R. Pereira, Toxicity of solid residues resulting from wastewater treatment with nanomaterials, *Aquat Toxicol*, 165 (2015) 172-178.
4. N. Adhoum, L. Monser, N. Bellakhal, J.-E. Belgaied, Treatment of electroplating wastewater containing Cu²⁺, Zn²⁺ and Cr(VI) by electrocoagulation, *Journal of hazardous materials*, 112 (2004) 207-213.
5. M. Hunsom, K. Pruksathorn, S. Damronglerd, H. Vergnes, P. Duverneuil, Electrochemical treatment of heavy metals (Cu²⁺, Cr⁶⁺, Ni²⁺) from industrial effluent and modeling of copper reduction, *Water research*, 39 (2005) 610-616.
6. H. Peng, J. Guo, Removal of chromium from wastewater by membrane filtration, chemical precipitation, ion exchange, adsorption electrocoagulation, electrochemical reduction, electrodialysis, electrodeionization, photocatalysis and nanotechnology: a review, *Environmental Chemistry Letters*, (2020).
7. A. Azimi, A. Azari, M. Reza kazemi, M. Ansarpour, Removal of Heavy Metals from Industrial Wastewaters: A Review, *Chem-BioEng Reviews*, 4 (2017) 37-59.
8. H. Xin, Q. Xinhong, C. Jinyi, Preparation of Fe(II)–Al layered double hydroxides: Application to the adsorption/reduction of chromium, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 516 (2017) 362-374.
9. R. Fu, X. Zhang, Z. Xu, X. Guo, D. Bi, W. Zhang, Fast and highly efficient removal of chromium (VI) using humus-supported nanoscale zero-valent iron: Influencing factors, kinetics and mechanism, *Sep Purif Technol*, 174 (2017) 362-371.
10. H. Peng, J. Guo, B. Li, Z. Liu, C. Tao, High-efficient recovery of chromium (VI) with lead sulfate, *Journal of the Taiwan Institute of Chemical Engineers*, 85 (2018) 149-154.
11. Y. Zhao, Removal of Chromium Using Electrochemical Approaches: A Review, *Int J Electrochem Sc*, 13 (2018) 1250-1259.
12. H. Peng, Y. Leng, J. Guo, Electrochemical Removal of Chromium (VI) from Wastewater, *Applied Sciences*, 9 (2019) 1156.
13. H. Peng, Y. Leng, Q. Cheng, Q. Shang, J. Shu, J. Guo, Efficient Removal of Hexavalent Chromium from Wastewater with Electro-Reduction, *Processes*, 7 (2019) 41.
14. Z. Zhao, a. He, J. Lin, M. Feng, V. Murugadoss, T. Ding, H. Liu, Q. Shao, X. Mai, N. Wang, H. Gu, S. Angaiah, Z. Guo, Progress on the Photocatalytic Reduction Removal of Chromium Contamination, *Chem Rec*, 19 (2019) 873-882.
15. X. Zheng, F. Kang, X. Liu, H. Peng, Z. JinYang, Carbon-coated Mg–Al layered double oxide nanosheets with enhanced removal of hexavalent chromium, *J Ind Eng Chem*, 80 (2019) 53-64.
16. X.Q. Liu, G. Zhang, H.Q. Xing, P. Huang, X.L. Zhang, Preparation of amphiphilic composite and removal of oil and hexavalent chromium from wastewater, *Environmental Chemistry Letters*, 9 (2011) 127-132.
17. C. He, L. Gu, Z. Xu, H. He, G. Fu, F. Han, B. Huang, X. Pan, Cleaning chromium pollution in aquatic environments by bioremediation, photocatalytic remediation, electrochemical remediation and coupled remediation systems, *Environmental Chemistry Letters*, 18 (2020) 561-576.
18. G.P. Gallios, M. Vaclavikova, Removal of chromium (VI) from water streams: a thermodynamic study, *Environmental Chemistry Letters*, 6 (2008) 235-240.
19. H. Peng, Q. Shang, R. Chen, L. Zhang, Y. Chen, J. Guo, Step-Adsorption of Vanadium (V) and Chromium (VI) in the Leaching Solution with Melamine, *Sci Rep-Uk*, 10 (2020) 6326.

-
20. J. Guo, R. Chen, L. Zhang, Q. Shang, Y. Chen, H. Peng, Adsorption of Chromium (III) on Melamine: Kinetic, Isotherm, Thermodynamics and Mechanism Analysis, *IOP Conference Series: Earth and Environmental Science*, 512 (2020) 012076.
 21. H. Peng, J. Guo, Reduction behavior of chromium(VI) with oxalic acid in aqueous solution, *Sci Rep-Uk*, 10 (2020) 17732.
 22. A. Ashiq, B. Sarkar, N. Adassooriya, J. Walpita, A.U. Rajapaksha, Y.S. Ok, M. Vithanage, Sorption process of municipal solid waste biochar-montmorillonite composite for ciprofloxacin removal in aqueous media, *Chemosphere*, 236 (2019) 124384.
 23. W.-H. Huang, D.-J. Lee, C. Huang, Modification on biochars for applications: A research update, *Bioresource Technol*, 319 (2021) 124100.
 24. X. Zheng, Y. Zhou, X. Liu, X. Fu, H. Peng, S. Lv, Enhanced adsorption capacity of MgO/N-doped active carbon derived from sugarcane bagasse, *Bioresource Technol*, 297 (2020) 122413.
 25. M.B. Ahmed, J.L. Zhou, H.H. Ngo, W. Guo, M.A.H. Johir, D. Belhaj, Competitive sorption affinity of sulfonamides and chloramphenicol antibiotics toward functionalized biochar for water and wastewater treatment, *Bioresource Technol*, 238 (2017) 306-312.
 26. R.R. Karri, J.N. Sahu, B.C. Meikap, Improving efficacy of Cr (VI) adsorption process on sustainable adsorbent derived from waste biomass (sugarcane bagasse) with help of ant colony optimization, *Industrial Crops and Products*, 143 (2020) 111927.
 27. M. Zubair, I. Ihsanullah, H. Abdul Aziz, M. Azmier Ahmad, M.A. Al-Harhi, Sustainable wastewater treatment by biochar/layered double hydroxide composites: Progress, challenges, and outlook, *Bioresource Technol*, 319 (2021) 124128.
 28. H. Peng, L. Yang, L. Wang, J. Guo, B. Li, Recovery of vanadium with urea in acidic medium, *Environmental Chemistry Letters*, 17 (2019) 1867-1871.
 29. H. Peng, Q. Shang, R. Chen, Y. Leng, J. Guo, Z. Liu, C. Tao, Oxidative Leaching Kinetics of Vanadium from the Vanadium-Chromium-Reducing Residue with K₂Cr₂O₇, *ACS Omega*, 5 (2020) 8777-8783.
 30. H. Peng, F. Wang, G. Li, J. Guo, B. Li, Highly Efficient Recovery of Vanadium and Chromium: Optimized by Response Surface Methodology, *ACS Omega*, 4 (2019) 904-910.
 31. H. Peng, L. Yang, Y. Chen, J. Guo, B. Li, Recovery and Separation of Vanadium and Chromium by Two-Step Alkaline Leaching Enhanced with Electric Field and H₂O₂, *ACS Omega*, (2020) 5340-5345.
 32. J.P. Gustafsson, Visual MINTEQ ver. 3.0, in, 2014.
 33. H. Peng, Q. Shang, R. Cheng, L. Zhang, Y. Chen, J. Guo, Highly efficient oxidative-alkaline-leaching process of vanadium-chromium reducing residue and parameters optimization by response surface methodology, *Environ Technol*, (2020) 1-10.
 34. V.A. Okello, S. Mwilu, N. Noah, A. Zhou, J. Chong, M.T. Knipling, D. Doetschman, O.A. Sadik, Reduction of hexavalent chromium using naturally-derived flavonoids, *Environmental Science and Technology*, 46 (2014) 10743-10751.
 35. X. Zhang, W. Fu, Y. Yin, Z. Chen, R. Qiu, M.-O. Simonnot, X. Wang, Adsorption-reduction removal of Cr(VI) by tobacco petiole pyrolytic biochar: Batch experiment, kinetic and mechanism studies, *Bioresour Technol*, 268 (2018) 149-157.
 36. G. Chen, J. Han, Y. Mu, H. Yu, L. Qin, Two-stage chromium isotope fractionation during microbial Cr(VI) reduction, *Water Research*, 148 (2019) 10-18.
 37. B. Chen, S. Huang, B. Liu, Q. Ge, M. Wang, X. Wang, Separation and recovery of vanadium and chromium from acidic leach solution of V-Cr-bearing reducing slag, *Journal of Environmental Chemical Engineering*, 5 (2017) 4702-4706.