Enhanced removal of hexavalent chromium from aqueous medium using highly stable and magnetically separable rosin-biochar-coated TiO$_2$@C nanocomposite

Balal Yousaf$^{a,b}$, Guijian Liu$^{a,b,*}$, Qumber Abbas$^a$, Ruwei Wang$^b$, Habib Ullah$^a$, Md Manik Mian$^a$, Amina$^c$, Audil Rashid$^d$

$^a$ CAS-Key Laboratory of Crust-Mantle Materials and the Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, PR China

$^b$ State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, The Chinese Academy of Sciences, Xi’an, Shaanxi 710075, China

$^c$ Environmental Ecology Laboratory, School of Resource and Environment, Anhui Agriculture University, Hefei 230026, PR China

$^d$ EcoHealth Research Group, Department of Environmental Sciences, PMAS Arid Agriculture University Rawalpindi, Pakistan

*Corresponding author’s:* lgj@ustc.edu.cn

Tel: +86-551-63603714; fax: +86-551-63621485
1. Kinetic models

1.1. Pseudo-first-order model: The linear/general form of the pseudo-first-order kinetic model to determine the adsorption capacity \( q_e \) of the RBC-TiO\(_2\)@C nanocomposites at equilibrium is as follows:

\[
\ln \left( \frac{q_e - q_t}{q_e} \right) = \ln q_e - \frac{k_1}{2.303}t
\]  

(3)

Where, \( q_e \) represents the adsorption capacity at equilibrium; \( q_t \) represents the adsorption capacity at time \( t \); \( k_1 \) represents the pseudo-first-order rate constant \( \text{min}^{-1} \). Values of both \( k_1 \) and \( q_e \) can be determined from the slope and intercept of linear \( \ln (q_e - q_t) \) vs. \( t \) plot.

1.2. Pseudo-second-order model: The linear/general form of the pseudo-second-order can be defined as below:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t
\]  

(4)

Where, \( k_2 = \text{pseudo-second-order rate constant} \ (\text{g mg}^{-1} \text{ min}^{-1}) \). Values of \( k_2 \) and \( q_e \) were determined from the slope and intercept of the linear plot between \( (t/q_t) \) vs. \( t \).

2. Adsorption study

Modeling of experimental adsorption isotherm data was performed using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherm models to provide the in depth information about adsorption behavior of RBC-TiO\(_2\)@C nanocomposites.

2.1. Langmuir isotherm model: Langmuir model describes the uniform surface of an adsorbent and assumes that an adsorbent contain the finite number of adsorption sites. This model describes monolayer adsorption of contaminants and uniform energetic forces of adsorption. Linearized form of Langmuir model is expressed as follows:

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e
\]  

(5)

where, \( K_L = \text{Langmuir constant} \ (\text{L mg}^{-1}) \); \( q_m = \text{maximum adsorption capacity} \ (\text{mg g}^{-1}) \); \( C_e = \text{concentration of Cr (VI) in solution at equilibrium} \ (\text{mg L}^{-1}) \); \( q_e = \text{amount of Cr (VI) adsorbed on} \)
the RBC-TiO$_2$@C nanocomposites at equilibrium (mg g$^{-1}$). The values of $q_m$ and $K_L$ can be calculated from the slope and intercept of linear $C_e$ vs. $C_e/q_e$ plot.

2.2. **Freundlich isotherm model:** This model describes multilayer or physisorption on the surface of the adsorbent (RBC-TiO$_2$@C). This model based on variable activation energy sites distributed on the adsorbent. Linear form of Freundlich model is as follows:

\[
\ln(q_e) = \ln(K_F) \cdot \frac{1}{n} \ln(C_e)
\]  

where, $1/n$ and $K_F$ are Freundlich empirical constants and their values can be evaluated from the slope and intercept of linear plot between $\ln(C_e)$ vs. $\ln(q_e)$.

2.3. **Temkin isotherm model:** This model describes the linear decrease in adsorption energy as with the coverage of adsorbent surface. Linearized form of Temkin model is as follows:

\[
q^e = \frac{RT}{b} \ln(K_T) + \frac{RT}{b} \ln(C_e)
\]  

Where $b$ (J mol$^{-1}$) and $K_T$ (L g$^{-1}$) are the Temkin isotherm constants, their values can be determined from slope and intercept of linear plot between $\ln(C_e)$ vs. $q_e$.

2.4. **Dubinin-Radushkevich (D-R) isotherm model:** This model provides the information about physical and multilayer adsorption. It assumes that van der Waals forces involved in adsorption. Linear form of D-R model is written as follows:

\[
\ln(q_e) = \ln(q_d) - \beta \varepsilon^2
\]  

\[
\varepsilon = RT \ln \left[ 1 + \frac{1}{C_{e_d}} \right]
\]

where, $q_d$(mg g$^{-1}$)= D-R constant; $\beta$ = constant related to free constant; $\varepsilon$ = Polanyi potential. The values of $\beta$ and $q_d$ can be calculated from the slope and intercept of linear $\varepsilon^2$ vs. $\ln(q_e)$ plot.
Table S1. Kinetic and equilibrium models, equations (General or non-linear form and Linear form), x and y values and, slope and intercept.

| Model               | Equation                                                                 | X and y value                      | Slope       | Intercept     |
|---------------------|--------------------------------------------------------------------------|------------------------------------|-------------|---------------|
| Pseudo first-order  | $\ln(q_e - q_t) = \ln q_e - \frac{k_1}{2.303}t$                        | $y = \ln(q_e - q_t)$, $x = t$     | $k_1$        | $\log q_e$    |
| pseudo second-order | $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}$                  | $y = \frac{t}{q_t}$, $x = t$     | $1$          | $\frac{1}{k_2 q_e^2}$ |
| Langmuir            | $\frac{C_e}{q_e} = \frac{1}{K_L q_m + q_m}$                            | $y = \frac{C_e}{q_e}$, $x = C_e$ | $\frac{1}{q_m}$ | $\frac{1}{K_L q_m}$ |
| Freundlich          | $\ln(q_e) = \ln(q_e) + \frac{1}{n} \ln(C_e)$                           | $y = \ln(q_e)$, $x = \ln(C_e)$   | $\frac{1}{n}$ | $\ln(K_F)$    |
| Temkin              | $q_e^e = \frac{RT}{b} \ln(K_T) + \frac{RT}{b} \ln(C_e)$               | $y = q_e^e$, $x = \ln(C_e)$       | $\frac{RT}{b}$ | $\frac{RT}{b} \ln(K_T)$ |
| Dubinin-Radushkevich (D-R) | $\ln(q_e) = \ln(q_d) - \beta \varepsilon^2$                         | $y = \ln(q_e)$, $x = \varepsilon^2$ | $\beta$ | $\ln(q_e)$    |

$q_e$ = adsorption capacity at equilibrium (mg g⁻¹); $q_t$ = adsorption capacity at time t (mg g⁻¹); $k_1$ = pseudo first-order rate constant (min); $t$ = time (min); $k_2$ = pseudo second-order rate constant (min); $C_e$ = Cr(VI) concentration in solution at equilibrium (mg L⁻¹); $q_m$ = maximum adsorption capacity (mg g⁻¹); $K_L$ = Langmuir adsorption isotherm constant (L mg⁻¹); $K_F$ = Freundlich adsorption isotherm constant (L g⁻¹); $n$ = heterogenuous factor of adsorption intensity; $b$ = Temkin constant for heat of adsorption (J mol⁻¹); $K_T$ = Temkin adsorption isotherm constant (L g⁻¹); $R$ = universal gas constant (8.314 J mol⁻¹ K⁻¹); $T$ = solution temperature (K); $q_d$ = Dubinin-Radushkevich (D-R) constant (mg g⁻¹); $\beta$ = D-R constant for free energy; $\varepsilon$ = Polanyi potential.
FigureS1. Comparative Cr(VI) removal efficiency of RBC and RBC-TiO$_2$@C nanocomposite (dosage @ 0.8 g L$^{-1}$) from aqueous solution (4 pH and 100 mg Cr(VI) L$^{-1}$) at 288 K temperature with 150 rpm shaking speed during 100 minutes of reaction time.
Figure S2. Comparative Cr(VI) removal efficiency of RBC-TiO$_2$@C nanocomposite under natural and artificial systems (dosage @ 0.8 g L$^{-1}$) from aqueous solution at 288 K temperature with 150 rpm shaking speed during 100 minutes of reaction time.
Figure S3. EDS results of biochar-coated RBC-TiO$_2$@C nanocomposite (a) before and (b) after Cr(VI) adsorption.
Fig S4. XPS spectra of spent biochar showing Cr(VI) reduction after fifth cycles.
Figure S5. Effect of coexisting ions (c = 100 mg L$^{-1}$) on the removal of Cr(VI) (c = 25 mg L$^{-1}$).