

Adsorption of hexavalent chromium using modified walnut shell from solution

Jingyi Li, Jie Ma, Qiehui Guo, Shenglong Zhang, Huayun Han, Shusheng Zhang and Runping Han

ABSTRACT

Modified walnut shell (MWS) was obtained using diethylenetriamine through a grafting reaction and its adsorption capacity toward Cr(VI) was enhanced. The adsorbent was characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and elemental analysis and the results showed that the modification was effective. To optimize experimental conditions, the effect of temperature, solution pH, salinity, contact time, and Cr(VI) concentration on adsorption quantity were performed in batch mode. It showed that the adsorption ability for Cr(VI) onto MWS can reach $50.1 \text{ mg}\cdot\text{g}^{-1}$ at 303 K with solution pH 3. Both the solution pH and salinity had a great impact on the adsorption capacity. The Langmuir model can predict the equilibrium process while the pseudo-second-order model can describe the kinetic process. The Yan model can be used to predict the column process. Additionally, there was also some regeneration ability for Cr-loaded MWS.

Consequently, MWS is effective for removing Cr(VI) from solution.

Key words | adsorption, hexavalent chromium, modified walnut shell, regeneration

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INTRODUCTION

Water is the source of life. With the rapid development of mining, electroplating, metallurgy and other industries, large amounts of industrial wastewater containing heavy metal ions such as lead, zinc, mercury and chromium have been discharged into various water bodies. The accumulation of heavy metal ions in the environment and the human body is possibly irreversible even at a trace level (Xu *et al.* 2020), and the pollution of water, air and soil has been a severe issue worldwide. Unlike organic contaminants, heavy metals are non-biodegradable, toxic and easily accumulated in the body through water (Fu & Wang 2011). The heavy metals commonly feature the atomic weights between 63.5 and 200.6 and specific gravities greater than 5.0, and there are about 60 kinds of metallic element (Srivastava & Majumder 2008). The World Health Organization (WHO) and Environmental Protection Agency (EPA) stipulate that the value of the maximum allowable emission volume of heavy metals into the environment is $2.0 \text{ mg}\cdot\text{L}^{-1}$ (Kurniawan *et al.* 2006; Hashim *et al.* 2011). However, large amounts of water with higher heavy metals concentrations, which surpass the allowable level, are still discharged into the

environment and create environmental pollution and serious disorders of human health (Carolin *et al.* 2017). Thus it is urgent to purify the water environment.

Because of corrosion resistance and aesthetic properties (Carolin *et al.* 2017), chromium and its compounds have many valence states, and the trivalent and hexavalent states have been widely used in industrial production. In these valence states, Cr(III) is a necessary trace element in mammals (Mohan & Pittman 2006), and the trivalent form is unstable and easily oxidized to a higher valence state in the oxic environment (Qi *et al.* 2016). But Cr(VI) is the most toxic valence state and easily absorbed by people, and shows strong carcinogenicity and mutagenicity. Therefore, it is necessary to find an effective method to remove the hexavalent chromium ion from water. Many methods have been developed to remove Cr(VI) from wastewater, including physical, chemical and biological techniques, such as adsorption (Lesmana *et al.* 2009), chemical precipitation (Boamah *et al.* 2015), reverse osmosis (Carolin *et al.* 2017), membrane filtration (Salehi *et al.* 2016), electrochemical treatment (Fu & Wang 2011), bioleaching process (Dinker & Kulkarni 2015) and so on.

Adsorption is one of the most commonly used methods of water treatment, with high efficiency, short cycle, good adaptability, easy operation and other advantages (Hua *et al.* 2012; Zhou *et al.* 2019). Currently, the adsorption of Cr(VI) in wastewater has been researched to some extent. For example, natural dolomite and wheat bran modified by tartaric acid have been used to adsorb Cr(VI) in wastewater (Albadarin *et al.* 2012; Kaya *et al.* 2014).

Compared with other types of adsorbents such as activated carbons, zeolites, fibers, organic resins and so on, biomass adsorbents from a variety of agro-forestry wastes have been used in water treatment in quantity because of the advantages of low costs, easy operations, being economically acceptable (Zhang *et al.* 2014) and having good availability (Wartelle & Marshall 2005). Some biomass materials naturally have an adsorption ability for contaminants, while others can be enhanced through a simple modification of surface functional groups to enhance their adsorption ability (Islam *et al.* 2019). For example, amine groups, quaternary ammonium and metal ions can improve sorption specificity and efficiency (Zhang *et al.* 2013; Xu *et al.* 2016).

Among a variety of biomass adsorbents, walnut shell (WS) could be used to remove dyes and heavy metal ions from water directly, due to its rich lignin, cellulose and hemicellulose (Yang *et al.* 2016; Liu *et al.* 2019). It also includes several functional groups like the carboxyl group and carbonyl and phenolic hydroxyl groups (Lu & Guo 2019). So, it can be widely used in the removal of heavy metal ions and dyes from solutions. For instance, Aguayo-Villarrel *et al.* (2013) used walnut shell to adsorb anionic dyes in water. Altun & Pehlivan (2012) used citric acid to modify walnut shell to improve the adsorption capacity for Cr(VI). Ding *et al.* (2014) used walnut shell modified by nickel chloride and potassium ferricyanide to prepare a new type of adsorbent, which showed satisfying adsorption performance on Cs^+ , and the adsorption rate was fast, up to adsorption equilibrium within 2 hours.

Amino modification may be an effective method to promote the adsorption ability of walnut shell. The amino groups existing in the surface of the adsorbent can bind heavy metal positive ions through complexation (Deng & Ting 2005). It can also adsorb anionic ions from solution through static-electric attraction with protonated amino

groups (Wang *et al.* 2013; Wang *et al.* 2016; Xu *et al.* 2016; Dong *et al.* 2019). The aim of this study was to prepare modified walnut shell (WS) by diethylenetriamine through grafting, and modified walnut shell (MWS) was obtained. The adsorption of Cr(VI) by MWS was performed. The breakthrough curve is also discussed. Finally, the regeneration performance of the adsorbent is explored.

MATERIALS AND METHODS

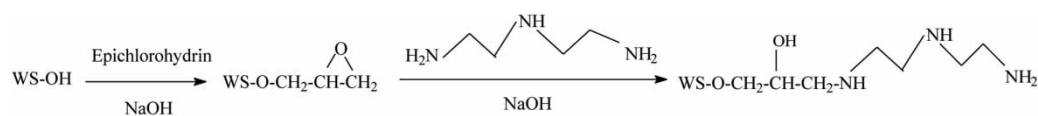
Materials

Walnut shell: the raw material was taken locally. After crushing and sieving, walnut shell was taken with particle size between 40 and 60 mesh, rinsed with deionized water, and dried to obtain the original walnut shell (WS).

Potassium chromate was used to prepare the adsorbate solution in the experiment and other common chemical reagents such as absolute ethanol (Fuchen Chemical Reagent, Tianjin, China), sodium hydroxide (Fuchen Chemical Reagent, Tianjin, China), sodium carbonate (Fuchen Chemical Reagent, Tianjin, China), epichlorohydrin (Kermel Chemical Reagent, Tianjin, China) and diethylenetriamine (Kermel Chemical Reagent, Tianjin, China) were all analytical grade.

Preparation of MWS

The walnut shell was modified by a grafting reaction; 5 g WS, 50 mL $2 \text{ mol}\cdot\text{L}^{-1}$ sodium hydroxide solution and 50 mL epichlorohydrin were added into a 250 mL Erlenmeyer flask, and the flask was placed in a thermostat oscillator and vibrated for 12 h at room temperature. Then, the mixtures were filtrated, and the solids were put in a new Erlenmeyer flask that containing 50 mL absolute ethanol, 50 mL diethylenetriamine, and a small amount of sodium carbonate. Next, the mixtures were vibrated for 12 h at room temperature to react completely. After that, the mixtures were filtrated and the obtained solids were washed several times by deionized water until neutral. Finally, the desired product, MWS, was dried at 40°C in an oven. The process is shown as below:



Characterization of WS and MWS

Several analytical techniques were used to characterize the adsorbents. The pH at point zero charge of MWS was evaluated by the 0.01 mol·L⁻¹ NaCl solid addition method. Fourier transform infrared spectroscopy (FT-IR Spectrometer, Nicolet iS50, USA) was used to identify the characteristic functional groups of WS and MWS. The content of nitrogen, carbon and hydrogen elements in WS and MWS were determined by automatic element analyzer (Flash EA 1122, Thermo Fisher Scientific). The crystal textures of WS and MWS were imaged by X-ray powder diffractometer (D/MAX-RA, Japan).

Adsorption experiments

Taken in series, a conical flask and 10 mL Cr(VI) solution (mass/solution volume, 50 mg·L⁻¹ or other concentration) and 0.010 g adsorbent were added in the flask, the conical flask was placed in the thermostatic oscillator (Guohua Enterprise SHZ-82, China) and vibrated for 6 h, filtered, and the residual Cr(VI) concentration of the solution was calculated by spectrophotometer (752, Shanghai Shun Yu Hengping Science Instrument Co., Ltd, China).

Influencing factors include: (1) effect of pH – the pH of the initial adsorbate solutions was controlled by 0.1 mol·L⁻¹ NaOH and HCl solution, (2) effect of salinity, (3) effect of adsorbate concentration and temperature – the initial concentrations of Cr(VI) were adjusted to 10–200 mg·L⁻¹, (4) effect of contact time and adsorbate concentration.

The adsorption quantity of Cr(VI) loaded onto unit weight of MWS was calculated using Equation (1):

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where V is the volume (L) of Cr(VI) solution, C_0 is the initial concentration (mg·L⁻¹) of Cr(VI), C_e is the concentration of Cr(VI) at any time t or equilibrium (mg·L⁻¹), and m is the mass of MWS (g).

Desorption study

A given mass of MWS was added to Cr(VI) solution, of which the concentration was 150 mg·L⁻¹, and which was shaken at a constant temperature of 303 K until the adsorption was saturated, filtered and dried, and then the desorption experiment was performed with 0.01 mol·L⁻¹ NaOH, and the desorption efficiency was calculated. After

that, Cr(VI) was re-adsorbed by the treated adsorbent, and the regeneration efficiency was calculated.

The desorption efficiency (d) and regeneration efficiency (η) were calculated using the following equations:

$$d = \frac{m}{m_c} \times 100\% \quad (2)$$

$$\eta = \frac{q_n}{q_e} \times 100\% \quad (3)$$

where m is the mass of Cr(VI) (mg) which is desorbed from the adsorbent and m_c is the remaining Cr(VI) mass on MWS before desorption (mg); q_n and q_e are the adsorption quantities of regenerative MWS for recycle times and the primitive MWS in the same experimental conditions, respectively.

Column adsorption

The adsorption experiment in a fixed-bed column was performed in one glass column (1 cm ID and 25 cm height), packed with 1.03 g MWS (height 2 cm). A solution with 30.0 mg·L⁻¹ Cr(VI) was pumped in downflow mode at flow rates of 8.0 mL·min⁻¹ using a peristaltic pump. Samples from the effluent were collected at regular intervals to measure the concentration of Cr(VI). Then the breakthrough curve ($C_t/C_0 \sim t$) could be obtained.

RESULTS AND DISCUSSION

Characterization of WS and MWS

The pH of point zero charge of WS and MWS in the solution is presented in Figure 1, which suggests that the

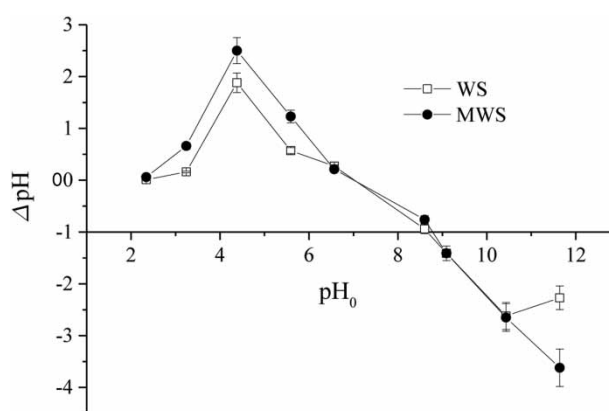


Figure 1 | The zero point charge of WS and MWS.

pH of point zero charge was basically unchanged, at pH 7. At pH < 7, the surface was positively charged in the solution while it was negatively charged at pH > 7.

Elemental analysis showed that the content of common elements was 48.4% for carbon and 6.02% for hydrogen in terms of WS, while it was 47.26% for carbon, 6.59% for hydrogen and the content of nitrogen increased from 0% to 1.69% regarding MWS, which confirmed that the amino groups were introduced onto the surface of WS successfully.

The X-ray diffraction (XRD) spectra of WS and MWS are shown in Figure 2. It was noticed that the positions of the diffraction peak were similar before and after the modification, indicating that the modification might have no great influence on the crystal structures. There were two characteristic diffraction peaks at about 22° and 16°, which represented highly ordered cellulose crystal structure and less-ordered polysaccharide structure respectively.

In order to determine the type of functional groups on the WS and MWS, FT-IR spectra were carried out and are shown in Figure 3. The wide absorption peak at 3,423 cm⁻¹ was due to the stretching vibration of -OH or -NH bonds. The strong peak of WS at 1,741 cm⁻¹ represented the stretching vibration of C=O in acetyl groups or carbonyl groups and the weakening of this peak from MWS was probably caused by a large amount of PEI which was on the surface of WS (Shang *et al.* 2016). The evident peak at 1,150 cm⁻¹ from the C-N stretching vibration indicated that PEI was introduced on the surface. The absorption peak at 1,244 cm⁻¹ was the characteristic absorption peak of the C-O-C stretching vibration in the alkyl aryl ether bond of WS. After modification, this peak was divided into absorption peaks of 1,228 cm⁻¹ and 1,267 cm⁻¹, and the

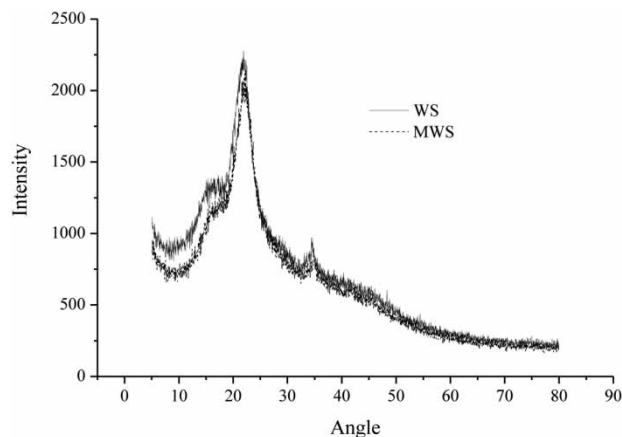


Figure 2 | XRD spectra of WS and MWS.

absorption intensity decreased to some extent. Relatively, the wide absorption peak near 1,038 cm⁻¹ represented the stretching vibration of the C-O bond in alcohol and the increase of the adsorption peak proved that the modification process changed some functional groups on the surface of the walnut shell.

The results from FT-IR and elemental analysis showed that MWS had some advantages in the adsorption of some pollutants.

Batch adsorption

The effect of pH on adsorption

The pH of the solution often plays an important role in the adsorption process and the effect is shown in Figure 4. When the pH value was in the range of 1–2, the unit adsorption capacity of Cr(VI) by MWS was about 22 mg·g⁻¹; then, q_e increased with the increasing pH, and the adsorption capacity reached 28 mg·g⁻¹ when the solution pH value was 3. With the continuous increase of the pH value, the adsorption capacity of Cr(VI) by MWS decreased gradually. At last, q_e was as low as 0.91 mg·g⁻¹ at pH 8. The chemical properties of Cr(VI) depend on pH value and its concentration. It is well known that the main form of Cr(VI) is HCrO₄⁻ when the pH value is less than 5. With the increasing of pH value, HCrO₄⁻ might shift to other forms, CrO₄²⁻ and Cr₂O₇²⁻ (Cimino *et al.* 2000). In aqueous solution, Cr(VI) mainly exists in the oxy-anion form. There was positive charge on the surface functional groups of the adsorbent like hydroxyl and amine groups due to protonation at lower pH. Thus, the main force between MWS and the Cr(VI) was electrostatic attraction. With the increase of the solution pH value, the degree of the protonation of functional groups in the adsorbent was decreased, which resulted in being less positively charged, and the HCrO₄⁻ might shift to CrO₄²⁻ and Cr₂O₇²⁻. So the electrostatic attraction was weakened and the adsorption capacity decreased. In order to facilitate the study of the adsorption behavior of Cr(VI) by MWS, the pH value of Cr(VI) solution was adjusted to 3 in subsequent experiments.

The effect of salinity on adsorption

The salinity also has a great impact on the adsorption quantity. The results are shown in Figure 5. The presence of salt had a negative influence on the adsorption quantity of MWS, and q_e gradually decreased with the increase of

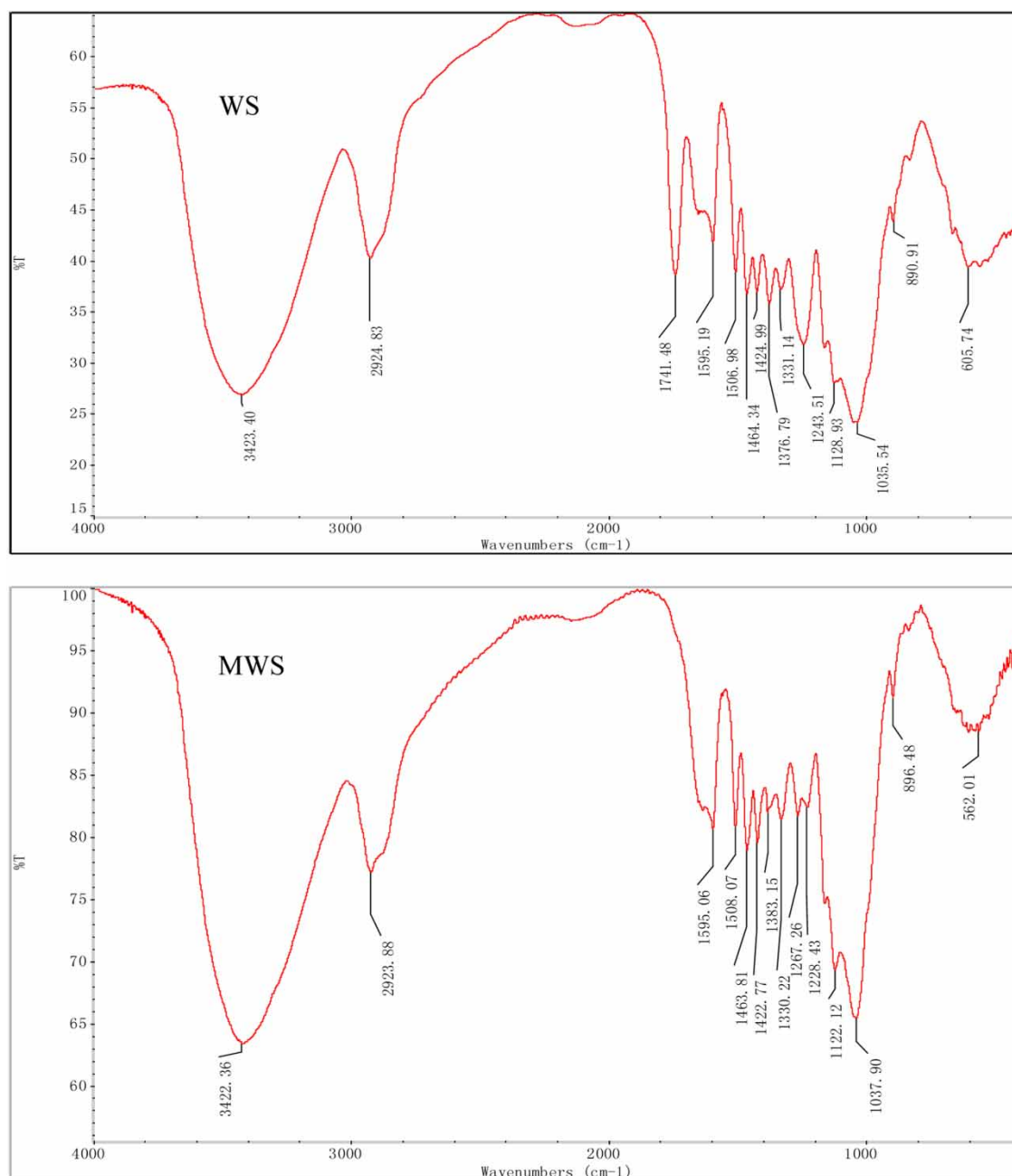


Figure 3 | FT-IR spectra of WS and MWS.

salt concentration. The addition of inorganic salts increased the ionic strength of the solution, reduced the activity coefficient, and the effective concentration of Cr(VI) was decreased, which might weaken the electrostatic attraction between MWS and Cr(VI). The anions in the salt solution might compete with Cr(VI) for the adsorption sites on the surface of MWS, which result in the decrease of adsorption capacity.

The effect of contact time on adsorption

Kinetic process is also important for adsorption. The effect of contact time on adsorption quantity is depicted in Figure 6. It is obviously shown in Figure 6 that a three-stage kinetic behavior was evidently observed for MWS: a rapid initial adsorption over 40 min (adsorption quantity: $19.9 \text{ mg}\cdot\text{g}^{-1}$), followed by a period of much slower uptake

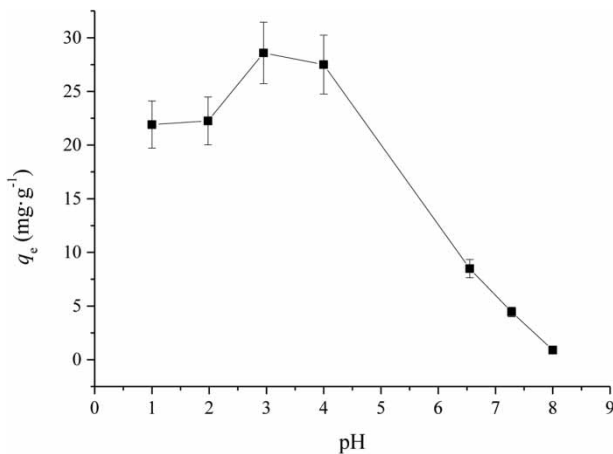


Figure 4 | The effect of solution pH on adsorption ($T = 303$ K, $C_0 = 50$ mg·L⁻¹, MWS dosage = 0.01 g, $t = 360$ min).

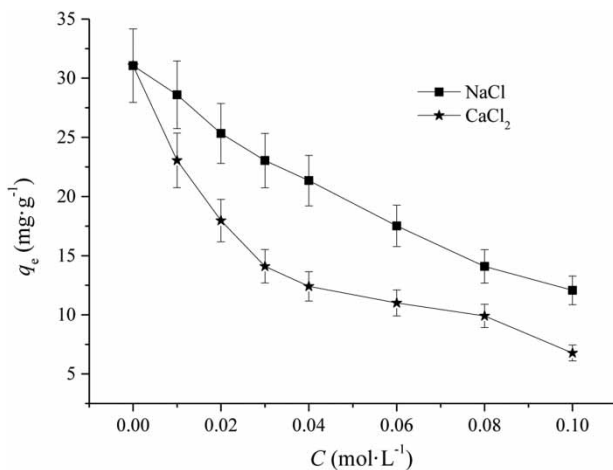


Figure 5 | The effect of salt concentration on adsorption ($T = 303$ K, $C_0 = 50$ mg·L⁻¹, MWS dosage = 0.01 g, $t = 360$ min).

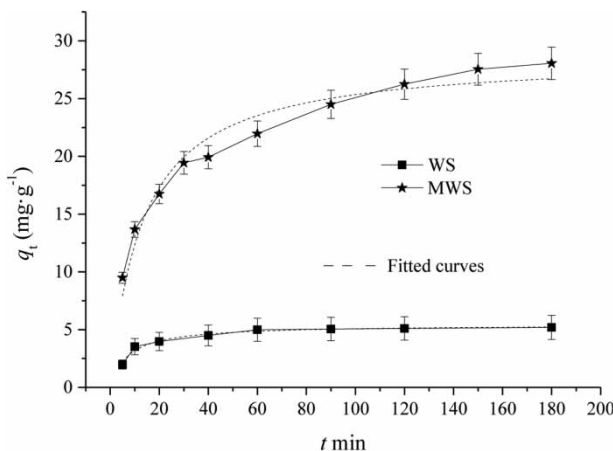


Figure 6 | Effect of contact time on adsorption quantity and kinetic fitted curves ($T = 303$ K, $C_0 = 50$ mg·L⁻¹).

of less than 150 min (27.5 mg·g⁻¹) and gradual equilibrium time to 180 min (28.0 mg·g⁻¹). At the initial stage of the reaction, the adsorption rate increased rapidly, which was probably because a large amount of Cr(VI) occupied the reaction sites on the surface of WS quickly. At the second stage, the adsorption sites became fewer, and the concentration of Cr(VI) also decreased. In addition, the absorbed Cr(VI) had a blocking effect on the absorption process, and therefore, the reaction rate became slow and reached equilibrium at the end.

For WS, a two-stage kinetic process was observed: fast at initial adsorption, then near equilibrium the adsorption quantity was only 5.20 mg·g⁻¹. So the adsorption capacity of MS toward Cr(VI) was significantly enhanced after amino introduction.

Kinetic analysis was performed and the pseudo-second-order kinetic model was used to fit the kinetic data:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (4)$$

where q_t is adsorption quantity (mg·g⁻¹) at time (t), q_e is adsorption quantity at equilibrium (mg·g⁻¹), and k_2 (mg·g⁻¹·min⁻¹) is the kinetic rate constant (Ho *et al.* 2000).

Nonlinear regressive analysis was applied to fit the data and the fitted results are presented in Table 1. The fitted curves are also presented in Figure 6.

It is noticed from Figure 6 and Table 1 that there are a higher determination coefficient (R^2) and lower values of SSE, and the values of q_e from the model are closer to the values of q_e from the experiments. Furthermore, the fitted curves are also closer to the experimental curves. So it could be concluded that the pseudo-second-order kinetic model can be used to predict the kinetic process of Cr(VI) adsorption onto WS and MWS. This model consists of all three steps of adsorption: (1) external film diffusion – transport of solute from bulk aqueous phase to the film of adsorbent molecules, (2) surface diffusion – diffusion of solute from the film to the pores of the adsorbent, and (3) intra-particle diffusion – adsorption of solutes onto the interior surface of the pores (Nethaji & Sivasamy 2014;

Table 1 | Parameters of pseudo-second-order kinetic model

	$q_e^{(exp)}$ (mg·g ⁻¹)	$q_e^{(cal)}$ (mg·g ⁻¹)	k_2 (g·mg ⁻¹ ·min ⁻¹)	R^2	SSE
WS	5.20	5.44 ± 0.12	0.0261 ± 0.0036	0.973	0.0381
MWS	28.0	28.7 ± 0.9	0.00266 ± 0.00044	0.960	1.69

Wu *et al.* 2015). It also showed that chemisorption may be the main rate-limiting step (Jung *et al.* 2013).

The effects of adsorbate concentration and reaction temperature on adsorption

The effects of Cr(VI) concentration and solution temperature on values of q_e were investigated, and the results are presented in Figure 7.

It is clearly noticed from Figure 7 that the value of q_e gradually increased with the increase of Cr(VI) equilibrium concentration, and the extent of increase was from fast to slow. Finally, the equilibrium adsorption capacity tended to a stable value, and the adsorption was basically at saturation. At different temperatures, three isotherms showed the same trend and the adsorption quantity was to 50.1, 51.1 and 52.8 mg·g⁻¹ from experiments at 303, 313, 323 K, respectively. So the higher temperature was in favor of Cr(VI) adsorption. However, the effect of temperature on the adsorption capacity was not significant.

The Langmuir model was used for the fitting analysis of the equilibrium data (Liu & Liu 2008; Zhao *et al.* 2017):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

where q_e is the equilibrium adsorption capacity (mg·g⁻¹), q_m is the maximum adsorption capacity (mg·g⁻¹), K_L is a constant related to the affinity of the binding sites and energy of adsorption (L·mg⁻¹), and C_e is equilibrium concentration (mg·L⁻¹).

The Langmuir model was used to fit the equilibrium data using nonlinear regressive analysis and the results are

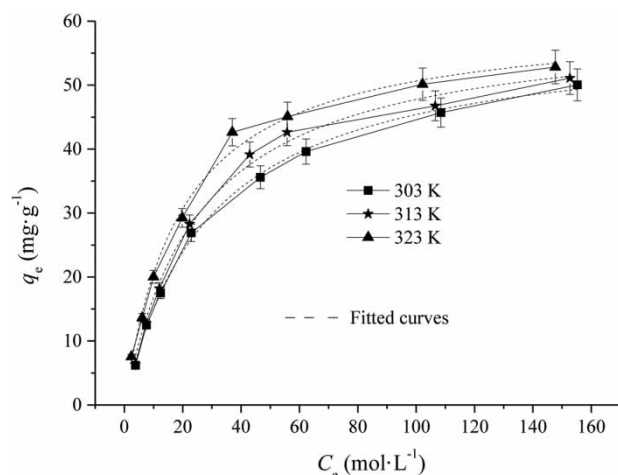


Figure 7 | Adsorption isotherms and Langmuir model fitted curves.

Table 2 | Parameters of Langmuir model of Cr(VI) adsorption onto MWS

T/K	K_L /(L·mg ⁻¹)	$q_{m(\text{exp})}$ /(mg·g ⁻¹)	$q_{m(\text{theo})}$ /(mg·g ⁻¹)	R ²	SSE
303	0.0346 ± 0.0016	50.1	58.5 ± 0.9	0.998	0.444
313	0.0389 ± 0.0033	51.1	60.0 ± 1.7	0.994	1.86
323	0.0516 ± 0.0046	52.8	60.4 ± 1.6	0.993	2.22

shown in Table 2. The fitted curves are also shown in Figure 7.

From the fitting results, the Langmuir model could well describe the adsorption process of Cr(VI) by MWS. The R² of the fitting were all over 0.99, and the errors were relatively small, and the maximum unit adsorption amounts calculated by the Langmuir model were also close to the experimental results. It was indicated that the adsorption of Cr(VI) could occur on the homogeneous surface by MWS through monolayer adsorption (Wang *et al.* 2018). Most of the adsorptions in accordance with the Langmuir model were chemisorption.

There have been many studies now on the adsorption capacity of Cr(VI) around the world. Table 3 lists the comparative data of adsorption capacity of Cr(VI) by various adsorbents in other studies. It can be seen that MWS has a good adsorption capacity toward Cr(VI) and there is some competence in application.

Calculation of thermodynamic parameters

The adsorption of Cr(VI) by MWS was an adsorption equilibrium process. In practice, it could be used to obtain the values of ΔG^0 , ΔH^0 , as well as ΔS^0 . The equilibrium constant (K_c) could be obtained according to the following Equation (6):

$$K_c = C_{\text{ad,e}}/C_e \quad (6)$$

Table 3 | The comparison of adsorption capacity of Cr(VI) with different adsorbents

Adsorbent	q_e (mg·g ⁻¹)	Reference
Dolomite	10.01	Albadarin <i>et al.</i> (2012)
Modified wheat bran	5.28	Kaya <i>et al.</i> (2014)
Green coconut shell	22.96	Kumar & Meikap (2014)
CA-WNS	30.99	Altun & Pehlivan (2012)
Activated carbon	6.01	Nethaji & Sivasamy (2014)
Surface modified nano-zeolite	14.16	Tashauoei <i>et al.</i> (2010)
MWS	50.1	This work

C_e and $C_{ad,e}$ are the concentrations of Cr(VI) in the solution as well as on MWS.

Calculating K_c , Equations (7) and (8) are used to get values of ΔG^0 , ΔH^0 , and ΔS^0 . Since the calculation of K_c requires the solution to be a very dilute ideal solution, which is difficult to achieve under experimental conditions, this paper used the several initial points on the isotherm to calculate $\ln K_c$, and then drew the line of C_e with $\ln K_c$. The intercept on the y-axis of the obtained line can be approximately considered as $\ln K_c$ under ideal conditions.

$$\Delta G^0 = -RT \ln K_c \quad (7)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (8)$$

where ΔG^0 means the Gibbs free energy (J), T denotes the absolute temperature (K), and R represents the gas constant (8.314 J·mol⁻¹·K⁻¹).

The thermodynamic parameters of adsorption were calculated and the results are shown in Table 4. It can be seen that the adsorption reaction was a spontaneous and entropy-increasing endothermic reaction. The change of enthalpy change was small during the adsorption process, indicating that the adsorption of Cr(VI) by MWS may be physical adsorption. In the adsorption kinetics analysis, the adsorption of Cr(VI) by MWS was consistent with the pseudo-second-order kinetic model, which indicated that there might be chemical reactions in the adsorption process. In the adsorption process, physical adsorption is often accompanied by chemical adsorption, so it was concluded that the adsorption process may have both chemical adsorption and physical adsorption.

Desorption and regeneration experiments

Recycling of adsorbent and recovery of adsorbate will make the treatment process economical (Han et al. 2010). Multiple regeneration experiments were conducted on MWS with 0.01 mol·L⁻¹ NaOH solution. The desorption efficiency of three regenerations was not high (19.5%, 20.9%, 18.0%), and the regeneration effect was also not good (71.8%,

60.7%, 51.2%). With the increase of regeneration time, the regeneration efficiency gradually decreased, which indicated that Cr(VI)-loaded MWS was not easily reused through regeneration. This implied the adsorption between Cr(VI) and MWS was probably dominated by chemical adsorption.

Column study

Continuous adsorption can be further performed in column mode. The breakthrough curve of Cr(VI) binding onto MWS is illustrated in Figure 8. It can be seen that the shape of the breakthrough curve was 'S' type. The breakthrough time ($t_{0.05}$) and half breakthrough time ($t_{0.5}$) (at time of $C_t/C_0 = 0.5$) were 18 min and 130 min, respectively.

The adsorption uptake ($q_{e(\text{exp})}$) was obtained using the following expression:

$$q_{e(\text{exp})} = \frac{vA}{1000m} = \frac{v}{1000m} \int_{t=0}^{t=t_{\text{total}}} (C_0 - C_t) dt \quad (9)$$

where v , t_{total} and A are volumetric flow rate (mL·min⁻¹), total flow time (min), and the area under the breakthrough curve, respectively; m is the dry weight of MWS (g).

According to Equation (9), the value of $q_{e(\text{exp})}$ was 31.2 mg·g⁻¹.

The Yan model was applied as the following expression (Yan et al. 2001; Song et al. 2011; Su et al. 2013):

$$\frac{C_t}{C_0} = 1 - \frac{1}{1 + (vt/b)^a} \quad (10)$$

where both a and b are parameters of the Yan model.

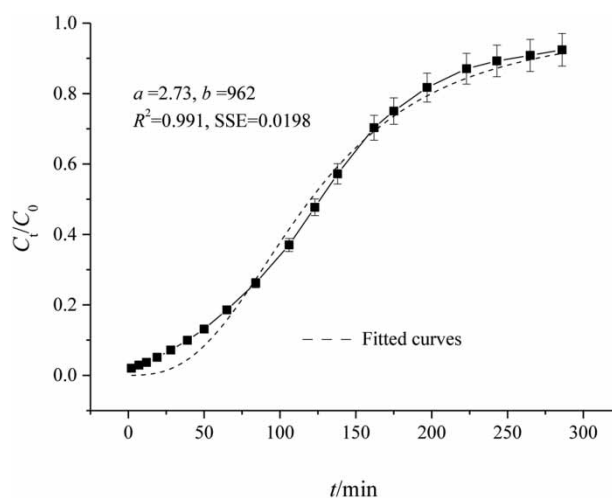


Figure 8 | Breakthrough curve and fitted curve of Cr(VI) adsorption on MWS (MWS 1.027 g, column height 2 cm, $C_0 = 30 \text{ mg}\cdot\text{L}^{-1}$, $v = 8 \text{ mL}\cdot\text{min}^{-1}$).

Table 4 | Thermodynamic parameters of adsorption

ΔH^0 /(kJ·mol ⁻¹)	ΔS^0 /(J·mol ⁻¹ ·K ⁻¹)	ΔG^0 /(kJ·mol ⁻¹)		
		303 K	313 K	323 K
15.7	56.4	-1.47	-1.76	-2.60

Using the nonlinear regressive analysis method, the values of a , b , determination coefficient (R^2), SSE and fitted curve are also shown in Figure 8. There was a higher value of R^2 and lower value of SSE, and the value of q_0 (bC_0/m) from the Yan model was $28.1 \text{ mg}\cdot\text{g}^{-1}$, smaller than $q_{e(\text{exp})}$. Furthermore, it can be observed from Figure 8 that the fitted curve was closer to the experimental curve. So the Yan model can be selected to predict the column process and adsorption quantity.

CONCLUSION

Compared with the WS, the adsorption performance of Cr(VI) by MWS was obviously improved. Solution pH value had a great influence and the presence of salt was not conducive to Cr(VI) adsorption. The adsorption isotherm was in accordance with the Langmuir model while the kinetic process was well fitted by the pseudo-second-order kinetic model. The Yan model could describe the column process well. As a consequence, MWS can be used to remove Cr(VI) from solution as a promising material.

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