

Effectiveness of Thermal and Acid Modification on Hexavalent Chromium Removal by Electrolyte Water Treatment Residuals

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A thermal and acid modification method was used to improve the Cr(VI) adsorption capability of electrolyte water treatment residuals (composed of aluminum electrolyte). The adsorbents were characterized by SEM, XRD, BET, and FT-IR to evaluate the adsorption capacity. Adsorption experiments were conducted as a function of pH, contact time, and concentration of Cr(VI). The optimal modification condition was a 1:1 solid-to-liquid ratio with 3.0-M hydrochloric acid after thermal modification. Both electrolyte water treatment residuals (E-WTRs) and thermal + acid modified (M-WTRs) were particularly effective for Cr(VI) removal under acidic conditions, with the most effective at pH 4.0. The adsorption of Cr(VI) reached equilibrium within 120 min and 300 min for E-WTRs and M-WTRs, respectively, with equilibrium absorption capacities of 9.89 mg/g and 14.63 mg/g. The reaction mechanism between the surface sites of WTRs and the Cr(VI) ions was a combination of anion exchange and surface complexation. The pseudo-second-order model is the most suitable for describing the adsorption kinetics for two adsorbents. The experimental equilibrium data can be interpreted by the Langmuir equation for E-WTRs and the Freundlich equation for M-WTRs.

Keywords: Electrolyte Water treatment residual solids; Modification; Hexavalent chromium; Adsorption; Desorption

1. INTRODUCTION

Rapid industrialization has led to an increased discharged wastewater containing heavy metals, which have detrimental effects on the environmental and human health. Chromium ions, which exist in both trivalent and hexavalent forms (Cr(III) and Cr(VI), respectively), are often present in the effluents of electroplating, tanning, mining, and fertilizer industries [1,2]. Cr(VI) is very toxic to humans and

animals due to its ability to diffuse freely across cell membranes and its high oxidation potential [3]. It can induce serious problems, such as bronchitis, bronchogenic carcinoma, liver damage, and ulcer formation [4,5]. As for the pollution hazards caused by Cr(VI), several removal methods have been reported, including co-precipitation, ion-exchange, reverse osmosis, photo-catalytic, adsorption, and electrochemical reduction [6-8]. In particular, adsorption is an economically feasible alternative due to its easy operation and the development of a variety of adsorbents. Although many adsorbents have been utilized for Cr(VI) removal, it remains important to develop alternative, more cost-effective adsorbents.

Electrolyte water treatment residual solids (E-WTRs), sometimes referred to as waterworks sludge, are a solid waste resulting from drinking water treatment processes. Typically, these residual solids contain by-products formed as followed: the addition of ferric or alum coagulants to remove colloids, silt and clay-size particles, and color during treatment; colloidal material and microbial species removed during treatment; and other chemicals used during treatment and/or species that were removed from the water during treatment [9-11]. Large quantities of these residual solids are generated by drinking water treatment plants, leading to research into the recycling of E-WTRs. Because of their amorphous nature, E-WTRs have a large surface area [12] and are highly reactive. Moreover, E-WTRs also consist of particles that settle as a result of coagulation and flocculation processes [13]. They have the proven ability to immobilize negatively charged ions, such as fluoride (F^-) [14], phosphate (PO_4^{3-}) [15], perchlorate (ClO_4^-) [16], arsenate (AsO_4^{3-}) [17], and selenium (as SeO_3^{2-} and SeO_4^{2-}) [18]. Cr(VI) exists mainly as $HCrO_4^-$, $Cr_2O_7^{2-}$, and CrO_4^{2-} in aqueous environments. Water treatment residuals may also adsorb Cr(VI) species, although this phenomenon and the bonding mechanisms have yet to be documented.

Appropriate pretreatment procedures can enhance an adsorbent's adsorption capability [19-21]. Therefore, the effectiveness of thermal and acid modification on Cr(VI) removal by E-WTRs was studied in this work. The effects of pH, initial Cr(VI) concentration, contact time, adsorption kinetics, adsorption isotherms, and desorption were investigated to determine the Cr(VI)-adsorption capabilities of the E-WTRs before and after modification. Scanning electronic microscopy (SEM), X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), specific surface area, and extraction toxicity experiments were also used to assess the influence of thermal and acid activation on the structure and stability of the E-WTRs. This work contributes to not only the improvement of the Cr(VI) adsorption capacity of the E-WTRs but also the promotion of their applications.

2. EXPERIMENTAL SECTION

2.1 Adsorbent preparation

E-WTRs were collected from a drinking water treatment plant that receives water from a reservoir in Harbin, China. This plant uses poly-aluminum chloride (PAC) as a coagulant for reducing turbidity and removing colloidal materials. Samples were placed in an oven and dried at 105 °C, then ground and sieved through a #100 sieve.

The modification method was as follows. First, E-WTR samples were placed in a quartz crucible and heated in a muffle furnace at 600 °C for 3 h. The samples were cooled and mixed in a desiccator. Next, the heated samples were mixed with 1.0-, 2.0-, and 3.0-M hydrochloric acid in a 1:1 solid-to-liquid ratio and stirred for 2 h. The mixtures were then dried at 60 °C. The modified samples were called M-WTRs. After modification, a standard adsorption experiment was developed to determine the best modification conditions and equilibrium time for further study. To this end, 0.3-g samples were placed into a series of 250-mL conical flasks. Next, 100 mL of 50-mg/L hexavalent chromium was added. The pH was maintained at 7 using NaOH or HCl, and samples were shaken for 24 h at 20 ± 1 °C. Thereafter, samples were filtered using 0.45- μ m Millipore filter paper. The residual chromium concentration in the solution was determined by UV-vis spectrophotometry (UV-160A, Shimadzu, Japan) at 540 nm following the 1,5-diphenylcarbazide method. Blanks were also run. The tests were repeated twice, and the average values were reported.

2.2 Adsorbent characterization

To investigate the surface morphology of the adsorbents, the samples were gold-coated by a sputter and observed using scanning electron microscopy (SEM: Tecnai G2 F30, USA). To determine the specific surface area (S_{BET}) of the adsorbents, the samples were analyzed with a surface area analyzer (ASAP 2020 M, Micrometrics Instrument Co.). The crystal structures of the adsorbent were analyzed by a powder X-ray diffractometer (XRD, D/max-rB 12KW, Japan). To qualitatively estimate the surface functional groups, the infrared spectra of the adsorbents were obtained by Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer Spectrum One B) in the range of 4000-400 cm^{-1} using the potassium bromide (KBr) pellet method.

The elemental contents of metals in the adsorbents were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 5300DU, Perkin Elmer Inc.). To understand the stability of the heavy metals in the E-WTRs (before and after modification), extraction toxicity experiments were conducted according to the Solid Waste-Extraction Procedure for Leaching Toxicity: Sulfuric Acid & Nitric Acid Method [22]. The results were compared with the Identification Standards for Hazardous Wastes: Identification for Extraction Toxicity [23] to determine whether they were hazardous materials.

2.3 Adsorption experiment

A stock solution of Cr(VI) was prepared by dissolving 2.8287 g of 99.9% potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in 1000 mL of distilled water. All working solutions of varying concentrations were obtained by successive dilution. The pH of the solution was adjusted to the required value using HNO_3 and NaOH. All the chemicals used were of analytical grade and were not purified further.

Adsorption experiments for E-WTRs and M-WTRs were undertaken by a batch equilibrium technique. The adsorption of chromium was performed by shaking a predetermined amount of adsorbent in a 100-mL chromium solution (with known initial chromium concentration and pH) at 150 rpm in a mechanically shaken water bath. After a given contact time, the solid material was separated

by centrifugation using a LG10-2.4A centrifuge at 7000 rpm. The residual chromium concentration in the solution was determined using a UV-vis spectrophotometer (UV-160A, Shimadzu) at 540 nm following the 1,5-diphenylcarbazide method [24].

The effect of pH on adsorption was investigated over the pH range of 3.0 to 9.0 (100-mL chromium solution, 50-mg/L initial metal concentration, 3.0-g/L adsorbent dosage, 20 ± 1 °C). After equilibrium was reached, the pH of the solution was measured and recorded. Contact time adsorption experiments were conducted at the optimal pH (obtained from the effect of pH) from 0 min to 360 min (100-mL chromium solution, 50-mg/L initial metal concentration, 3.0-g/L adsorbent dosage, 20 ± 1 °C). Sorption isotherms were obtained for initial metal concentrations varying from 20 to 400 mg/L at the optimal pH (100-mL chromium solution, 3.0-g/L adsorbent dosage, 20 ± 1 °C).

The adsorption capacity, q_t (mg/g), was determined from the difference between the initial chromate concentration (C_0 , mg/L) and the concentration at time t or at equilibrium (C_t , mg/L) per gram of solid adsorbent:

$$q_t = (C_0 - C_t) \cdot V / m \quad (1)$$

Where m is the mass of adsorbent (g) and V is the volume of solution (L).

2.4 Desorption and regeneration

For the desorption study, Cr(VI)-loaded E-WTRs were prepared by bringing E-WTRs into contact with Cr(VI) solution to achieve a Cr(VI) concentration of 50 mg/L and were equilibrated for 7 d. The amount of Cr(VI) adsorbed was determined by analyzing the dried Cr(VI)-loaded E-WTRs for total Cr concentration.

The desorption of Cr(VI) was studied by adding dried Cr-loaded E-WTRs in a 1:20 (m/v) ratio to an extracting solution with a final pH of 4.22. The extracting solution was prepared according to the US-EPA Synthetic Precipitation Leaching Procedure (SPLP) [25]. Next, the samples were rotated in capped centrifuge tubes at approximately 150 rpm for 7 d, and the supernatant was analyzed for total Cr. The percentage of Cr(VI) desorbed was calculated using equation (2):

$$\% \text{Cr desorbed} = C_{des} V / m C_{ads} \times 100\% \quad (2)$$

Where C_{des} is the desorbed Cr concentration in the SPLP extracting solution (mg/L), C_{ads} is the Cr adsorbed concentration on E-WTRs (mg/kg), V is the volume of extracting solution (mL), and m is the weight of E-WTRs (g).

3. RESULTS AND DISCUSSION

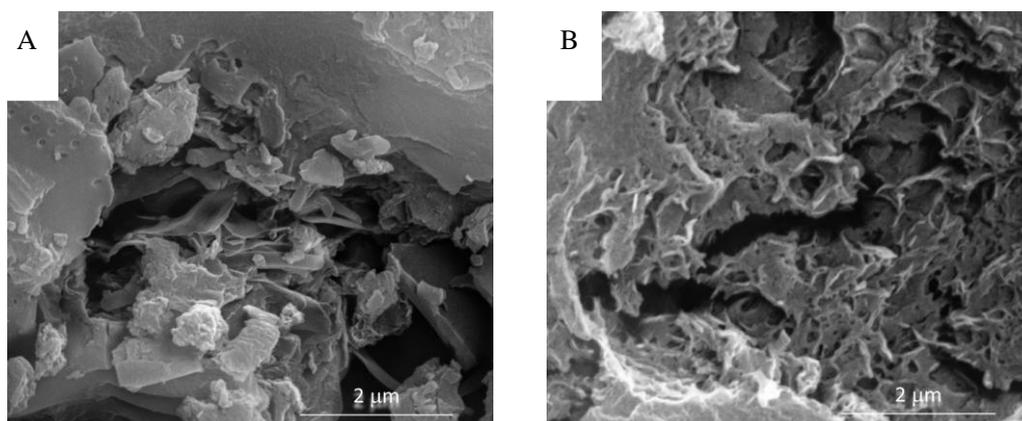
3.1 Characterization of the E-WTRs

The total contents of Al and Fe in E-WTRs and M-WTRs were determined (Table 1). The results show that the total Al and total Fe contents increased after modification from 162.7 to 266.9 mg/g and from 44.4 to 73.2 mg/g, respectively. pH_{IEP} decreased slightly, from 5.4 to 4.2. The specific surface area decreased substantially, from 84.02 to 25.36 m^2/g .

Table 1. Major elemental composition and chemical properties of E-WTRs and M-WTRs

Parameter	E-WTRs	M-WTRs
Total Al (mg/g)	162.7	266.9
Total Fe (mg/g)	44.4	73.2
pH _{IEP}	5.4	4.2
S _{BET} (m ² /g)	84.02	25.36
Total pore volume (cm ³ /g)	0.08	0.04

The results of the SEM, XRD, and FT-IR analyses of the E-WTRs before and after modification are shown in Figures 1(A&B), 2, and 3, respectively. The surface structures were changed by the modification (Figure 1(A&B)); the adsorbent surface underwent carbonization during the thermal process.

**Figure 1.** SEM patterns of E-WTRs (A-before modification; B-after modification).

According to the XRD results, the E-WTRs contained quartz, feldspar, calcite, and kaolinite and the M-WTRs contained aluminum iron oxide crystal and quartz (Figure 2). Both the Al and Fe in the E-WTRs existed in amorphous forms before modification. No difference in the peak position of the FT-IR patterns was found between E-WTRs and M-WTRs (Figure 3), except for the peak at 1408 cm⁻¹, which disappeared after modification. The peak positions in the FT-IR pattern indicated the composition of the tested substances, and the amplitudes reflected the relative content levels of different components. The E-WTRs are physical mixtures of aluminum and iron hydrolysate (oxides) containing small quantities of activated carbon and polymer. Therefore, it is difficult to clearly confirm the compositions at the wavelengths of approximately 1400 cm⁻¹, 1600 cm⁻¹, and 3400 cm⁻¹. The structures of the E-WTRs before and after modification were similar, but their contents have changed. The decreased contents in the M-WTRs may be due to the loss of impurities in the E-WTRs because of the thermal treatment.

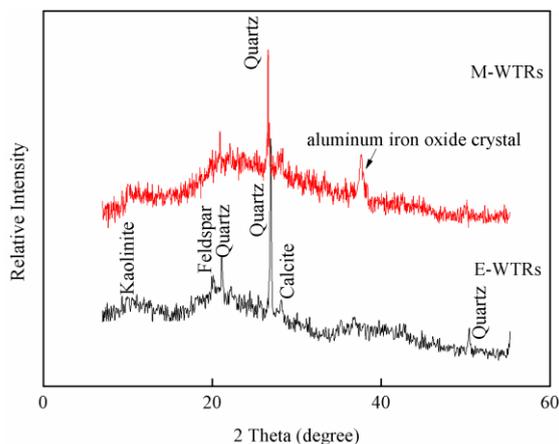


Figure 2. X-ray powder diffraction patterns of E-WTRs and M-WTRs.

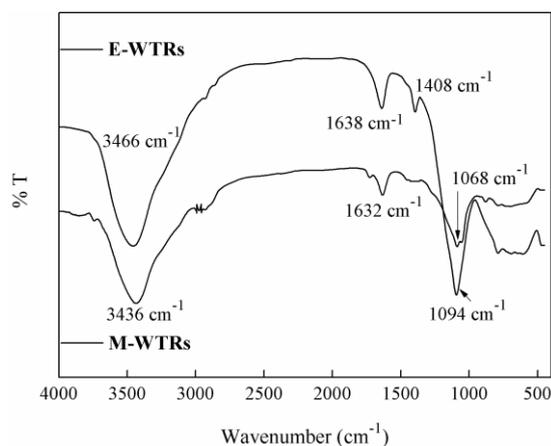


Figure 3. FT-IR patterns of E-WTRs and M-WTRs.

Extraction toxicity results are listed in Table 2. The results indicate that among silver (Ag), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), and mercury (Hg), only Cd and Zn were released from the E-WTRs, and As, Cr, Cd, Cr, Ni, Pb, and Zn were released from the M-WTRs in slightly higher levels compared with E-WTRs. However, the amounts of the heavy metals released were below the standard for extraction toxicity [23]. Therefore, both E-WTRs and M-WTRs were relatively safe Cr(VI) adsorbents.

Table 2. Results of extraction toxicity of E-WTRs before and after modification (Units: mg/L)

Sample	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
E-WTRs	ND	ND	0.05	ND	ND	ND	ND	ND	0.013
M-WTRs	ND	0.36	0.17	0.57	0.18	ND	0.18	0.38	1.48
Standard	5.00	5.00	1.00	15.00	100.00	0.10	5.00	5.00	100.00

ND=not detected

Standard=hazardous wastes standard

3.2 Effect of modification

The effect of modification of E-WTRs on the adsorption of Cr(VI) ions is presented in Figure 4. The adsorption capacity was reduced by the thermal modification, which may be attributed to the increase in temperature causing a decrease in the surface area as amorphous Al and Fe transform into mineral crystals in the E-WTRs (see Figure 4). The acid treatment increased the adsorption capacity of E-WTRs for Cr(VI) ions, which might be attributed to the acid-neutralizing part of the negative charge of the E-WTRs surface and might generate positively charged sites (protonation of -OH groups) [26]. This enables the reaction with the negatively charged HCrO_4^- ions and thus tends to increase the adsorption. The optimal concentration for the acid modification on E-WTRs was determined to be 3.0 M.

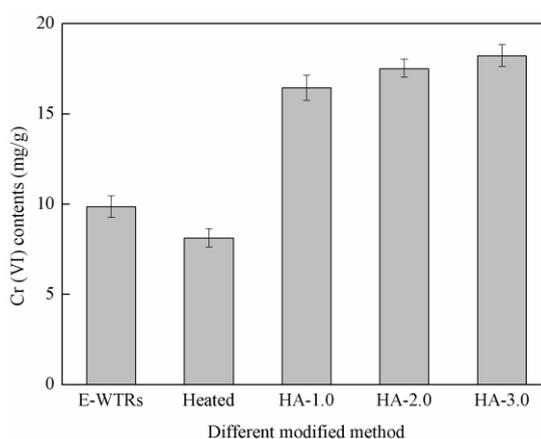


Figure 4. Effectiveness of Cr(VI) adsorption with different modification conditions. (Heated: thermally modified E-WTRs; HA: E-WTRs modified by sequential thermal and acid modification; 1, 2, and 3: acid concentration in M).

3.3 Effect of pH

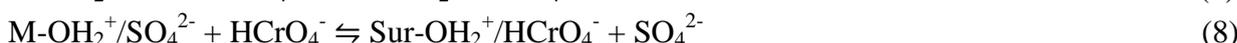
The results of Cr(VI) adsorption before and after modification under different pH conditions are shown in Figure 5A. When the initial pH increased from 3.0 to 9.0, the Cr(VI) adsorption capacities of the E-WTRs and M-WTRs decreased from 9.89 to 2.65 mg/g and from 14.63 to 4.27 mg/g, respectively. Both the E-WTRs and M-WTRs had the highest adsorption capabilities at pH 4.0. The equilibrium pH values were always higher than the initial pH values.

In aqueous solution, Cr(VI) exists in different ionic forms depending on both the pH and total Cr(VI) concentration [27]. It exists in five main forms in aqueous solution. Among these forms, the most important Cr(VI) states in solution are chromate (CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$), and hydrogen chromate (HCrO_4^-) (Figure 5B), for which the equilibrium reactions are as shown in equation (3), (4), and (5), respectively [28,29]. From Figure 5B, HCrO_4^- and CrO_4^{2-} are the most prevalent species at the total Cr(VI) concentration used in the experiment[30].





The pH at which the zeta potential equals zero is called the isoelectric point (IEP) and it can be used to qualitatively assess the adsorbent surface charge and characterize the protonation and deprotonation of the amphoteric surface functional groups. At values below the pH_{IEP} , the hydrated surface of the adsorbent is protonated, thereby acquiring a positive charge. At pH values higher than the pH_{IEP} , the hydrated surface of the adsorbent is deprotonated, thereby acquiring a negative charge. The pH_{IEP} values of E-WTRs and M-WTRs are 5.4 and 4.2, respectively. Therefore, at values below the pH_{IEP} , there may be two possible mechanisms for Cr(VI) adsorption onto E-WTRs and M-WTRs. The primary mechanism is anion exchange, wherein the OH^- , Cl^- , and SO_4^{2-} ions associated with the surface of the adsorbent exchange with the Cr(VI) molecules in solution [31], which may be written as



By determining the Cl^- and SO_4^{2-} contents in the solution before and after the reaction, it was found that the concentration of Cl^- and SO_4^{2-} in solution increased. This finding indicates that ion exchange is the main mechanism behind the removal of Cr(VI).

Another possible mechanism is surface complexation, which is suggested for anion adsorption onto metal oxides and hydroxides. The formation of surface complexes such as $\text{CrO}_4^{2-}/\text{Al}_2\text{O}_3$, $\text{CrO}_4^{2-}/\text{AlOOH}$, and $\text{CrO}_4^{2-}/\text{FeOOH}$ was verified in previous studies [32,33]. The association between the positively charged surface of the adsorbent and the HCrO_4^- anions may be written as



Under alkaline conditions, CrO_4^{2-} is now the dominant species and the surface of the adsorbent is deprotonated and acquires a negative charge; thus, although the adsorption affinity of CrO_4^{2-} is higher than that of OH^- , the CrO_4^{2-} must compete with the OH^- in the solution for anion exchange sites and the amount adsorbed decreases. This result is in agreement with previous studies [34]. In addition, the equilibrium pH value is higher than the relevant initial pH. It is inferred that anion exchange could release OH^- (see equation 6).

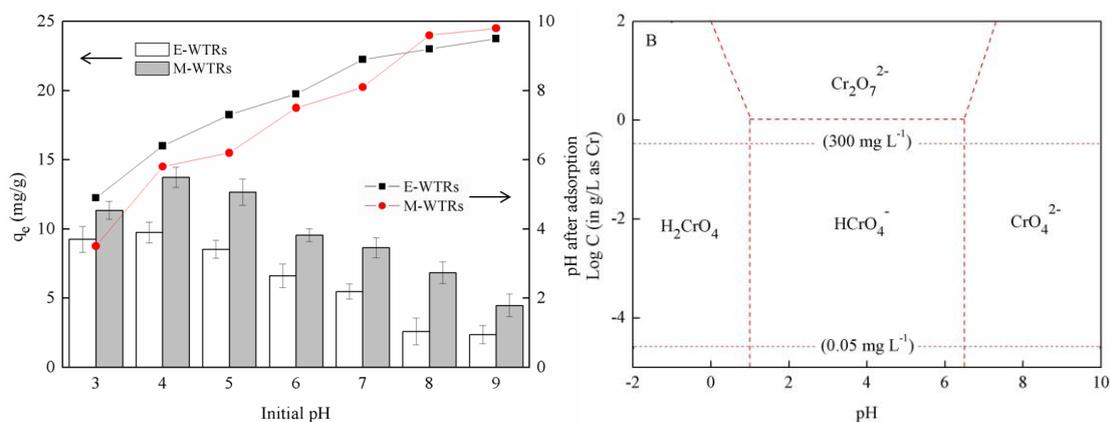


Figure 5. Effect of initial pH on adsorption and equilibrium pH (A) and the predominance diagram showing the relative distribution of different Cr(VI) species in water as a function of pH and total Cr(VI) concentration (B).

3.4 Effect of contact time and dynamics study

The adsorption processes were studied as a function of time to determine the point of equilibrium using adsorption experiments of Cr(VI) ions onto E-WTRs and M-WTRs. All experiments were run triplicate, and a good reproducibility of the procedures was obtained. The results are shown in Figure 6(A). The adsorption of Cr(VI) ions onto M-WTRs is rather rapid, and after 300 min, the adsorption equilibrium is achieved. E-WTRs also adsorb Cr(VI), requiring 120 min to achieve adsorption equilibrium, but the removal rate is lower compared than that of the M-WTRs. The amount of Cr(VI) ions removed reached a maximum of 9.89 mg/g and 14.63 mg/g for the E-WTRs and M-WTRs, respectively.

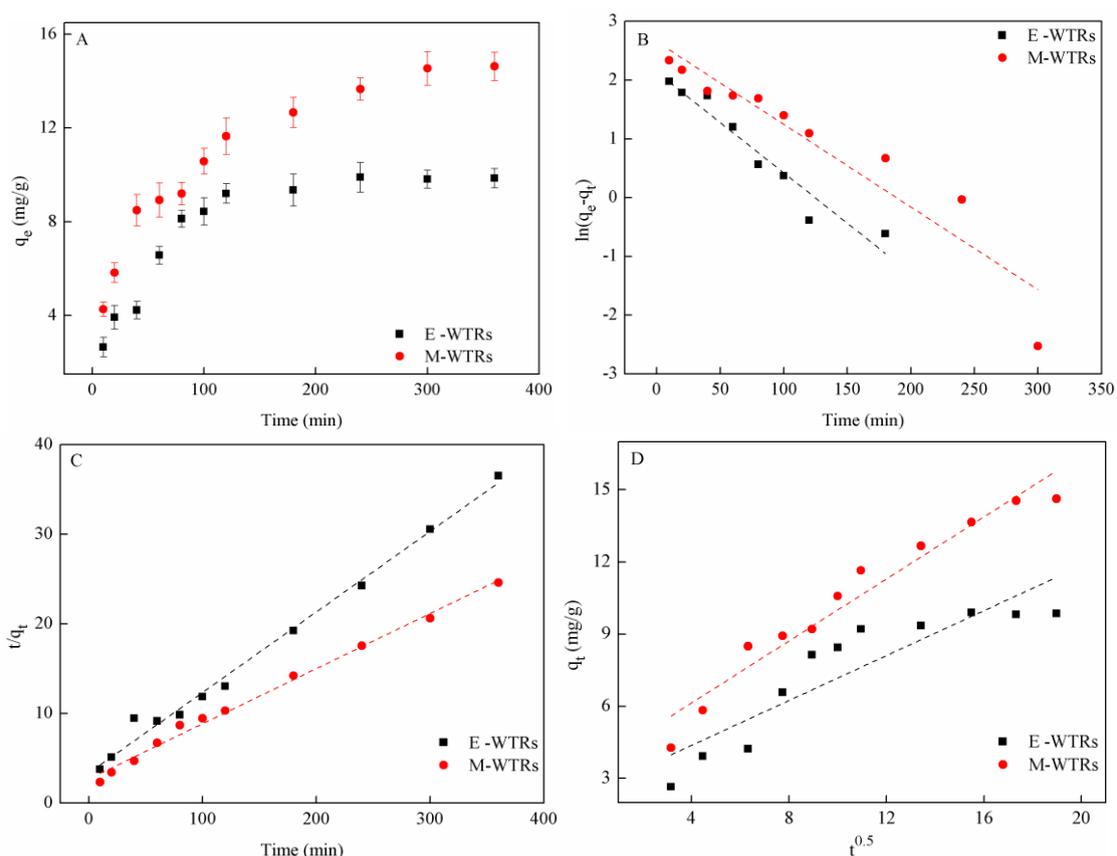


Figure 6. Effect of contact time on the uptake of Cr(VI) (A), pseudo-first-order kinetic plot (B), pseudo-second-order kinetic plot (C), intra-particle diffusion kinetic plot (D).

Kinetic modeling not only allows the estimation of the adsorption rates but also yields rate expressions that can be used to identify possible reaction mechanisms. In this respect, several kinetic models, including the pseudo-first-order equation (Figure 6B), pseudo-second-order equation (Figure 6C) [35] and intra-particle diffusion mode (Figure 6D) [36], were tested.

The calculated kinetic parameters for Cr(VI) adsorption are listed in Table 3. Of the three kinetic equations tested, the pseudo-second-order model is the most suitable for describing the

adsorption kinetics of Cr(VI) on E-WTRs and M-WTRs, as determined by the correlation coefficient (R^2). This finding suggests that chemical reactions play an important role, featuring the ion exchange between Cr(VI) with surface ligands (such as OH^- , Cl^- , SO_4^{2-}) to form covalent bonds with amorphous hydroxyl-Al and Al lattice ions.

Table 3. Fitting results of the experimental adsorption kinetics of E-WTRs and M-WTRs.

Models	Parameters	E-WTRs	M-WTRs
Pseudo-first-order $\ln(q_e - q_t) = \ln q_e - k_1 t$	$k_1 (\times 10^{-3} \text{ min}^{-1})$	17.07	14.08
	$q_e (\text{mg/g})$	8.46	14.23
	R^2	0.9237	0.8841
Pseudo-second-order $t/q_t = 1/k_2 q_e^2 + t/q_e$	$k_2 (\times 10^{-3} \text{ g/mg}\cdot\text{min})$	2.41	1.41
	$q_e (\text{mg/g})$	2.3095	2.6249
	R^2	0.9903	0.9925
Intra-particle $q_t = k_i t^{0.5} + C$	k_i	2.51	3.56
	C	0.47	0.64
	R^2	0.7941	0.9435

3.5 Effect of initial concentration and adsorption isotherm

Initial concentration is an important factor in adsorption efficiency. Experiments to study the effect of initial concentration were performed with variable initial chromium concentrations (20, 50, 100, 200, 300, and 400 mg/L). Cr(VI) adsorption increased with increasing equilibrium concentration of the metal ion and tended to plateau as the adsorbent became progressively saturated (Figure 7(A&B)). To determine the Cr(VI) adsorption characteristics of the E-WTRs before and after modification, Langmuir, Freundlich, and Temkin models were used to fit the experimental data. The results are listed in Table 4.

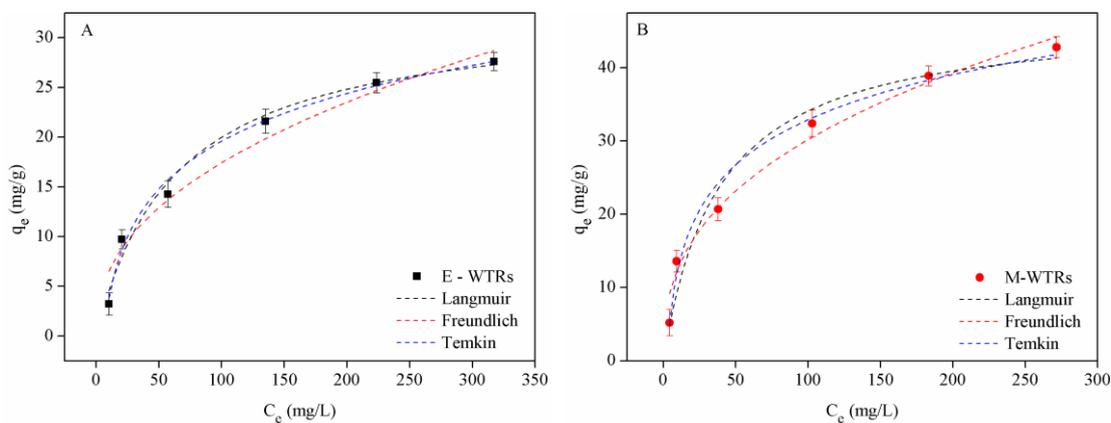


Figure 7. Cr(VI) adsorption isotherms of E-WTRs (A) and M-WTRs (B)

Table 4. Fitting results of the experimental adsorption isotherms of E-WTRs (A) and M-WTRs

Model	Parameters	E-WTRs	M-WTRs
Langmuir $q_e = q_m k_L C_e / (1 + k_L C_e)$	k_L (L/mg)	0.0155	0.0263
	q_m (mg/g)	32.787	47.1007
	R^2	0.9829	0.9605
Freundlich $q_e = k_F C_e^{1/n}$	k_F (mg/g)	2.371	5.2265
	n	2.3095	2.6249
	R^2	0.9589	0.9771
Temkin $q_e = B_1 \ln(k_T + C_e)$	k_T (L/g)	0.1675	0.4067
	B_1	6.9512	8.8847
	R^2	0.9618	0.9589

Table 4 presents the parameters of the Langmuir, Freundlich, and Temkin isotherms, revealing that the isotherm data for E-WTRs is best fitted to the Langmuir model, which provides the best results based on the correlation coefficient ($R^2=0.9829$). The results are in agreement with those previously reported by other authors for Cr(VI) adsorption tests [37]. The saturated adsorption capacities (q_m) of the Cr(VI) by E-WTRs at $20 \pm 1^\circ\text{C}$ are 32.787 mg/g. The isotherm data for M-WTRs have been fitted to the Freundlich model, yielding a correlation coefficient (R^2) of 0.9771. The slope $1/n$ is the adsorptive intensity, where $n > 2$ is interpreted as an indication of an adsorbent with good adsorbent characteristics for the solute being considered [38]. In this study, the values of n are 2.3095 and 2.6249 for E-WTRs and M-WTRs, respectively, which indicated that the M-WTRs exhibited better affinity than E-WTRs for Cr(VI); the Cr(VI) binding capability of the M-WTRs was stronger. B_1 in the Temkin model corresponds to the adsorption heat. In this study, the B_1 of the M-WTRs was greater than that of the E-WTRs, which most likely indicated that the adsorption activity was higher for the M-WTRs [39].

3.6 Desorption

Desorption was studied by the leaching of the formed Cr-[E-WTRs] complexes with synthetic acid solutions, which led to the release of 9.5% and 1.5% of Cr previously sorbed onto the E-WTRs and M-WTRs, respectively. Although preliminary, these results suggest that the leaching potential of Cr from E-WTRs could be very low. E-WTRs therefore have potential applications for heavy metal immobilization.

4. CONCLUSION

The adsorption of Cr(VI) from the aqueous state onto E-WTRs and M-WTRs was studied under various conditions. The M-WTRs were better able to remove Cr(VI) than the E-WTRs. Both E-

WTRs and M-WTRs had the highest adsorption capabilities at pH 4.0, and the mechanisms of Cr(VI) adsorption were ion exchange and surface complexation. The pseudo-second-order model is the most suitable for describing the adsorption kinetics of Cr(VI) onto E-WTRs and M-WTRs. The experimental equilibrium data can be interpreted by the Langmuir equation for E-WTRs and the Freundlich equation for M-WTRs. The E-WTRs could be used for the removal of toxic Cr(VI) ions present in aqueous states for pollution control.

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