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ORIGINAL ARTICLE

A novel nanocomposite-based zeolite for efficient remediation of Cd-contaminated industrial wastewater

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Abstract

Novel nanocomposite sorbent was produced by depositing nanostructured water treatment residual (nWTR) onto zeolite (Ze) using high-energy ball milling process. The physicochemical properties of nanocomposite (Ze-nWTR) prior and after Cd adsorption were analyzed by SEM–EDX, FTIR, BET and XRD. A batch study of cadmium adsorption (Ze-nWTR) was performed at various process parameters (sorbent dose, contact time, solution pH, competing ions, initial concentration and temperature). The obtained data were fitted to various equilibrium and kinetics models. The Langmuir and power function models successfully described Cd adsorption equilibrium and kinetic processes, respectively. The maximum adsorption capacity (q_{max}) value of Cd by Ze-nWTR nanocomposite (147 mgg^{-1}) was 3 and 5.9 times higher than those of nWTR and zeolite sorbents, respectively. Increasing temperature from 287 to 307 K has resulted in increasing the maximum Cd adsorption capacity (q_{max}) of the nanocomposite from 147.9 to 270 mgg^{-1}. The calculated thermodynamics parameters suggested physical and chemical attraction between Cd and Ze-nWTR and the association of dissociative mechanism in Cd(II) sorption process. The excellent reusability and Cd removal ability of Ze-nWTR nanocomposite (98%) from industrial wastewater confirm its potential as promising adsorbent for wastewater treatment applications.

Keywords Ze-nWTR · Nanocomposite · Adsorption/kinetic · Thermodynamics · Reusability · Industrial wastewater

Introduction

Recently, surface water and groundwater contamination with heavy metals is worldwide serious environmental concern (Kumar et al. 2021; Hussain et al. 2019a). Sewage from different industries such as cadmium–nickel batteries, plastic manufacturing, melting and casting industries, electroplating, pesticides, mining, petroleum refining processes, and photography is considered the main resource of heavy metals release in the environment. At extremely low concentrations, heavy metal can seriously damage public health and aquatic life (Mehta et al. 2015). Cadmium (Cd^{2+}) has caught the attention of academia and industry because of its carcinogenic effect and common use in industrial applications (Rangel-Porras et al. 2010; Pinto 2019). Therefore, seeking a suitable approach to remediate Cd-contaminated wastewater is urgently needed.

Because adsorption technique is considered the best choice over further traditional techniques in wastewater treatment field (Jia et al. 2019; Tavker et al. 2021), optimization of inexpensive and effective sorbent materials is a major challenge in developing the most efficient technology for heavy metals removal (Hussain et al. 2017; Ahmed et al. 2020; Liu et al. 2022). Zeolite is a cheap natural aluminum silicate mineral that widely studied because of its high affinity to adsorb heavy metals (Li et al. 2011; Ngah et al. 2013; Peng et al. 2021). Similarly, millions of tons of water treatment residual (WTR), byproducts of drinking water industry, are generated every day and released to the environment from water treatment facilities. Recently, these bulk waste materials have converted to nanoparticles by physical approaches (Elkhatib et al. 2015) and proven to be one of the low cost and efficient sorbents due to their specific and strong binding to Hg and Cr (Elkhatib et al.

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2017, 2019; Moharem et al. 2019). The WTR nanoparticles also demonstrated high removal efficiency for Cd from aqueous solution as the adsorption capacities of nWTR were 17 and 10 times higher than those of bulk WTR in single- and multi-element systems, respectively (Elkhatib et al. 2016). However, flow rate through nWTRs system in fixed bed column is low because of separation difficulty of solid–liquid phase as a result of its ultrafine particle size (El-Kammah et al. 2022).

In recent years, the role of composites in water purification have drawn the attention of researchers and environmentalist due to their high selectivity and decontamination ability in removal of various pollutants (Herrera-Barros et al. 2020; Ajala et al. 2022; Hussain et al. 2019b). Pandey et al. (2017) have used zeolite-supported microscale zero-valent iron (Z-mZVI) to remove Cd and Cr from aqueous solution. They indicated that the adsorption capacity of Z-mZVI composite for Cr and Cd much exceeded the removal capacity of either nanoscale zero-valent iron (nZVI) or zeolite. Similarly, Angaru et al. (2021) reported that fly ash-based zeolite decorated with nano-ZVI and Ni-bimetallic have been proven to be highly efficient in removal of heavy metals from industrial effluents. Furthermore, coating zeolite surface with Al–iron oxides nanoparticles enhanced the r eactivity and zeolite adsorption affinity for heavy metals (Nguyen et al. 2015). Thus, zeolite can be easily modified to improve the relative adsorption capacity toward heavy metals (Bowman 2003; Akhigbe et al. 2016; Li et al. 2019; Khulbe and Matsuura 2018). However, information on the capability of zeolite-supported nWTR (Ze-nWTRs) in heavy metals removal under different environmental conditions in batch and in column adsorption systems are not available and need investigation. In this study, a novel composite sorbent (Ze-nWTR) was produced by depositing nWTR onto zeolite to get the maximum benefit of the two sorbents for removal of Cd from wastewater. Thus, the current study objectives were to: (1) synthesize and characterize a zeolite–nWTR nanocomposite (Ze–nWTR), (2) assess Ze–nWTR nanocomposite efficiency for Cd removal from wastewater through batch and column experiments, (3) demonstrate Cd sorption behavior by Ze-nWTR under various conditions of solution pH, coexist competing ions, sorbent dose, temperature and contact time and (4) elucidate removal mechanism of Cd from aqueous solution by the nanocomposite.

Materials and methods

Source/synthesis of (Ze-nWTR) composite

The bulk drinking water treatment residual (WTR) was collected from Kafr El-Dawar water purification plant in El-bohera, Egypt. Physio-chemical characteristics of WTRs are presented in Table (S1) (Supplementary materials). The WTR samples were air-dried, ground and passed through two different 2 mm and 51 µm diameter stainless steel sieves. The WTRs were milled into nanoscale particles using the Fritsch planetary mono mill technique (Elkhatib et al. 2015). The natural zeolite was purchased from Delta Biotec company (Borg Alarab, Egypt). The natural zeolite certified analysis is shown in Table (S2). The zeolite samples were dried at 80 °C for 24 h., ground and sieved with a 100 mesh screen before use. The composites were prepared by ionizing 1.0 g zeolite with $NaNO_3$ 0.1 M for one week, and finally dried. The coating process of clay/nWTR (*w*/*w*) mixture was in a ratio of 2:1 and 4:1. The mixture was treated with ultrasound for 30 min and then vigorously stirred at room temperature for 120 min. The black solid product was washed five times with a (1:1) ethanol /water solution, dried and then stored.

Characterization

Emission scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectra (EDX) was used for characterization of nWTR, zeolite and Ze–nWTR nanocomposite. Surface area of the three studied sorbents was measured by N_2 adsorption using surface area and porosimetry (SAP) analyzer (Brunauer et al. 1938). The KBr pellets were used for recording Fourier transform infrared (FTIR) spectra of the sorbent powders before and after Cd sorption.

Kinetics of Cd adsorption

Adsorption experiments were performed in polyethylene tubes (50 mL) by adding 0.2 g zeolite, nWTR or Ze-nWTR composite into 20 mL Cd^{2+} solution of certain concentrations at 25 °C and placed on a shaker of 170 rpm for different time intervals (5 min–24 h). Samples were withdrawn at each time intervals, centrifuged for 10 min at 4000 rpm and filtered through a Millipore filter (0.45 µm). The total amount of Cd concentrations in the filtered solution was determined using atomic absorption spectrometer (contrAA 300). The sorption data were applied to different kinetic models (First-order, Elovich, Intraparticle diffusion model, and modified Freundlich).

Adsorption isotherms

Equilibrium sorption experiments were performed by adding 0.2 g of zeolite, nWTR, or Ze-nWTR composite to 20 mL of ($CdCl_2{\cdot}2H_2O$) solution with a concentration range of 40–800 mgL^{-1}. After stirring at 170 rpm at 25 °C for 20 h, solution samples were collected, centrifuged,

filtered, and analyzed for total Cd as previously stated in the kinetics section. Adsorption data were fit seven isotherm mathematical models (Langmuir, Freundlich, Elovich, Temkin, Fowler–Guggenheim (FG), Kiselev, and Hill de Boer). The thermodynamic parameters of the Ze-nWTR composite were calculated by applying the Arrhenius equation to the sorption data obtained at three different temperatures (287, 297 and 307 K), three pH values (4, 7 and 9) and different Cd concentrations (100), 250, 500 and 1000 mg L^{-1}).

To evaluate the effect of coexisting ions on Cd adsorption by Ze-nWTR, a similar series of adsorption experiments were performed in the presence of three competing cations (Ni, Zn, Cu) at an initial Cd(II) concentration of 500 mg L^{-1}. Additionally, to investigate the effect of adsorbent dose on Cd removal, the same adsorption experiments were performed using three different adsorbent weights (0.1, 0.2, and 0.3 g) of each adsorbent at an initial Cd concentration of 500 mg L^{-1}.

The thermodynamic study

The changes in Gibbs free energy ($\Delta G°$, J mol^{-1}), enthalpy ($\Delta H°$, J mol^{-1}) and entropy ($\Delta S°$, J mol^{-1} K^{-1}) were determined to grasp the explanatory effect of temperature on Cd adsorption process. These parameters were determined by the following equations:

$$\Delta G° = -RT \ln K_c \quad (1)$$

$$K_c = C_{qe}/C_S \quad (2)$$

where R = gas constant [8.314 kJ/(molK)], K_c = equilibrium constant, C_{qe} = amount of Cd(II) adsorbed from solution to adsorbent at equilibrium (mg L^{-1}), C_S = equilibrium concentration of Cd(II) in solution (mg L^{-1}).

To obtain C_{qe} and C_S, we used qe from the Langmuir model.

$\Delta H°$ and $\Delta S°$ were calculated from the $\Delta G°$ and T plot (Fig. 8) using the following equations:

$$\Delta G° = \Delta H° - T\Delta S° \quad (3)$$

Reuse of Ze-nWTR adsorbent composite

The reusability of the Ze-nWTR nanocomposites was evaluated for six cycles using 0.01 M HCl solution. The nanocomposites loaded with Cd were dried, soaked in 50 mL of HCl (0.01 M) and stirred for 120 min at room temperature. The suspension was then filtered, dried, and the recovered nanocomposite was reused for Cd removal. The adsorption–desorption process was repeated for six cycles.

The Cd adsorptive removal efficiency of nanocomposite

Bach study

The efficiency of Ze-nWTR nanocomposite for Cd(II) removal was evaluated by set up a batch experiment using real wastewater from Al-Bilali agricultural drainage and industrial effluents of paper manufacturing factory (Rakta). The chemical analysis of the wastewaters used in the study is presented in Table (S3). Because the agricultural drainage sample was free of cadmium, it was spiked with 5 mg L^{-1} Cd.

The efficiency of Cd removal by nanocomposites

Bach study

The effectiveness of Ze-nWTR nanocomposites for removal of Cd(II) was evaluated by conducting batch experiments using real wastewater from Al-Bilali agricultural wastewater and industrial wastewater from a paper mill (Rakta). The chemical analysis of the wastewater used in the study is shown in Table (S3). Because agricultural drainage samples were Cd free, 5 mg L^{-1} Cd was added to the industrial effluent samples.

Column experiment

Column tests were presented to investigate the efficiency of nanocomposites for Cd removal from real wastewater. Experiments were conducted in a flow reactor contained a mixture of Ze-nWTR composite and sand. A PVC column with a height of 20 cm and an inner diameter of 2.5 cm was used to test the filter medium, i.e., a homogeneous mixture of Ze-nWTR composite and sand at certain mass ratios. A peristaltic pump continuously supplied the pollutant containing solution to a reservoir connected to the column. The solution passed through the column by gravity, and the effluent was periodically collected and analyzed. A schematic diagram of the experimental column is shown in Figure (S1) (Supplementary Material).

Results and discussion

Surface appearance and chemical structure of the adsorbent

nWTR

The nWTR particles are predominantly spherical in the size range 45–96 nm, as shown in Fig. S2; elemental

analysis (SEM–EDX) showed that nWTR contained Fe, Si, and Al in proportions of 49.57, 21.77, and 6.3% of the total elements, respectively. In addition, X-ray diffraction analysis confirmed that amorphous iron, aluminum (hydr) oxide, and silicon oxide mainly existed in the crystalline iron-Al(hydr)oxide-free nWTR (Fig. S2).

Zeolite

As seen in the SEM image (Fig. 1a), the zeolite particles are mostly spherical in the size range of 20–28 nm. As a result of SEM–EDX elemental analysis, O, Si, Al, and Fe accounted for about 91% of all zeolitic elements, and C, Ca, K, Fe, and Mg accounted for 9%.The XRD pattern

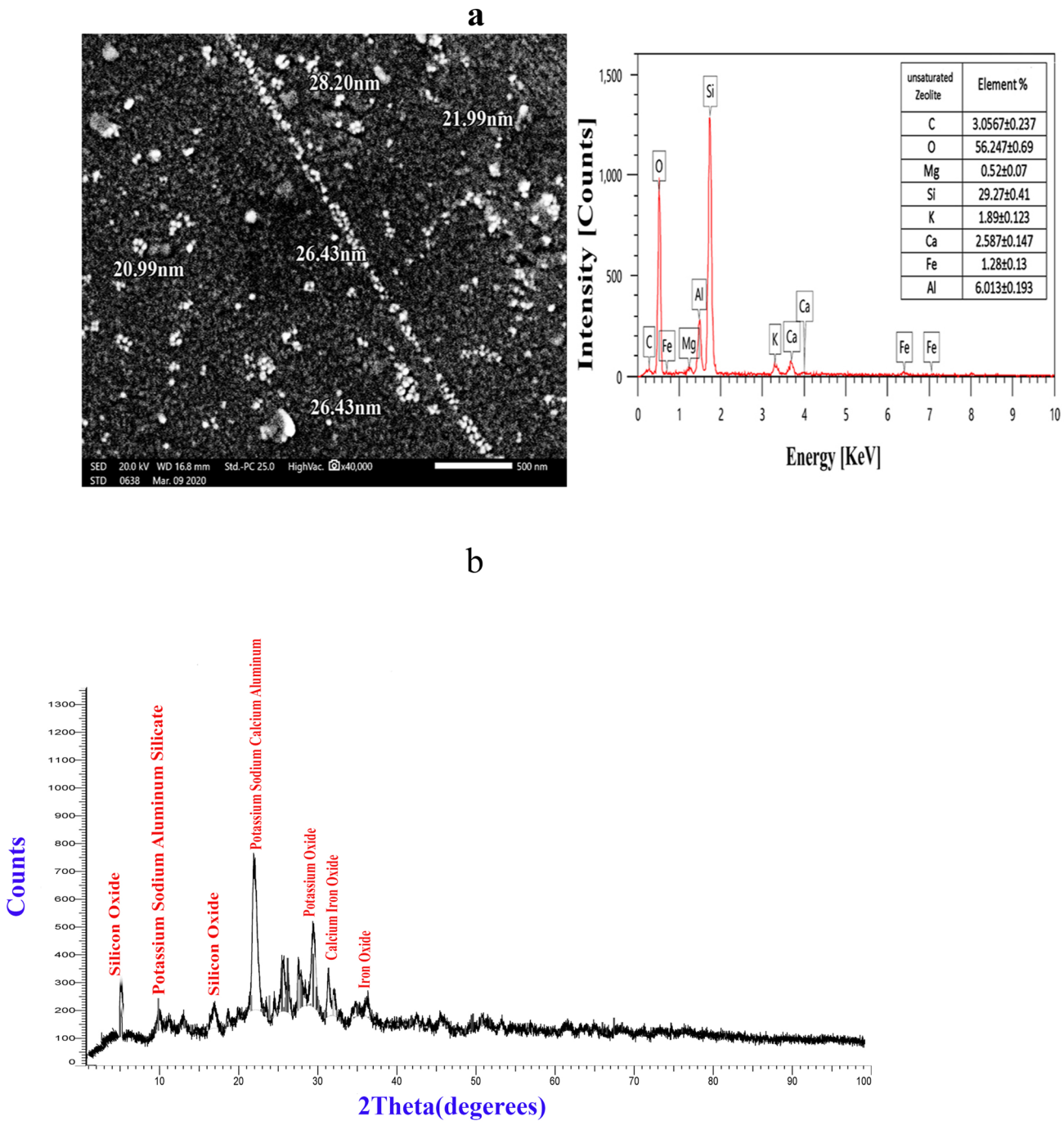


Fig. 1 Scanning electron microscopy (SEM) image and energy-dispersive X-ray (EDX) spectrum (**a**) and X-ray diffraction (XRD) analyses of zeolite (**b**)

of zeolite (Fig. 1b) shows strong characteristic peaks at $2\theta = 4.5$ and 67.861, indicating that the zeolite sample contains a large proportion of silica (SiO2). Additionally, the peaks appearing at 2θ values of 9.4 and 25 indicate the presence of potassium sodium aluminum silicate, while the peaks appearing at 2θ values of 21.3 and 27.3 belong to potassium sodium calcium aluminum. Moreover, peaks with 2θ values of (31.8 and 40), (35.021 and 46.5) and (41.9 and 76.5) indicate the presence of calcium iron oxide, iron oxide and potassium oxide, respectively.

Ze-nWTR nanocomposite

The morphology of the surface microstructure of the nanocomposite is shown in Fig. 2a. SEM images show that zeolite flakes and nWTR spherical nanoparticles are dispersed on the zeolite surface. The diameter of the spherically dispersed particles is in the nanoscale range (51.02–71.43 nm), and the presence of these nanoparticles on the surface of the zeolitic clay can prevent the agglomeration of these particles. According to EDX analysis, O, Si, C, Al and Fe, K and Na are the main elements in the nanocomposite, accounting for about 98% of the total element concentration. The minor components of the nanocomposite are Ca, Mg, Cu, and Cr, which are 0.81, 0.51, 0.83, and 0.51%, respectively. The presence of Al and Fe indicates the presence of nano-WTR and may increase the Cd removal capacity of the Ze-nWTR nanocomposite. SEM–EDX elemental analysis of Cd-loaded Ze-nWTR nanocomposite is shown in Fig. 2b. Among the detected elements, the appearance of the cadmium peak (3.08%) is evidence of the successful loading of Cd into the Ze-nWTR nanocomposite. XRD pattern of Ze-nWTR (Fig. 2c) shows characteristic peaks at $2\theta = 9.48$ and 12.81, indicating the presence of potassium and sodium aluminosilicate in the Ze-nWTR sample. The appearance of peaks at 2θ values of 12.7 and 28.6 indicates the presence of sodium potassium manganese oxide, while the peaks at 2θ values of 22 and 27.7 belong to calcium aluminum silicate. Iron, aluminum, chromium oxide and iron, aluminum, chromium, copper have 2θ values (36.1 and 58.3) and (44.7 and 64.7), respectively.

Specific surface area (SSA)

The nWTR and the zeolite specific surface area (SSA) were determined. The nWTR SSA (129 m^2g^{-1}) is much higher than that of the zeolite sample (39 m^2g^{-1}). The SSA of the Ze-nWTR nanocomposite was found to be 89 m^2g^{-1}. Certainly, nWTR can provide additional available surface sites for Cd adsorption on high SSA nanocomposites.

Fourier transmission infrared spectroscopy

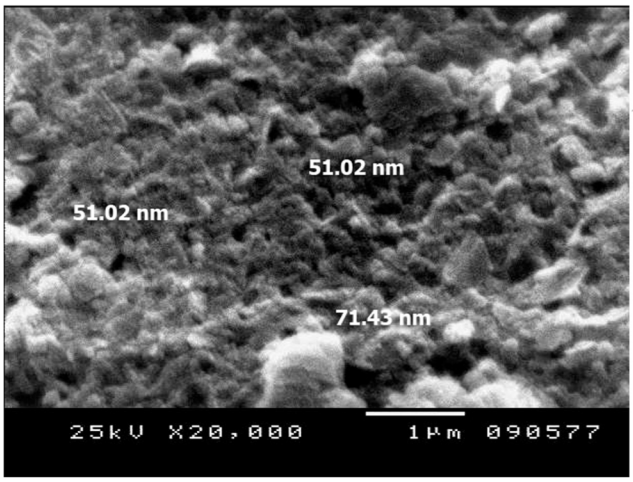
FTIR spectrum of Ze-nWTR (Fig. 3a) showed a strong broad band at 3424 cm^{-1} attributed to the O–H bending vibration and a small band at 1638 cm^{-1} associated with the H–O–H molecular bending mode (Ruan et al. 2002). In addition, the main band at 1044 cm^{-1} assigned to the FeOH vibration of feroxyhyte and the band at 466 cm^{-1} assigned to the O–AL–O stretching vibration are shown in Fig. 3a (Carlson and Schwertmann 1981). The retention of Cd on the Ze-nWTR surface loaded with Cd results in significant spectral changes. The shift of the band from 3424 to 3438 cm^{-1} and the increase in intensity confirm the participation of surface hydroxyl groups in the Cd adsorption process. Similarly, the band at 1638 cm^{-1} shifts to 1634 cm^{-1} and increases in intensity. The band shift and intensity increases from 1044 to 1045 cm^{-1} and the band shift from 466 to 475 cm^{-1} are clear evidences of specific molecular interactions. Therefore, OH, O–Al–O, FeOH and FeO(OH) structures are proposed to participate in the Cd adsorption process by Ze-nWTR nanocomposites. The FTIR spectra of nWTR or Cd-loaded/unloaded zeolites are shown in Fig. 3b, c, respectively. After Cd adsorption, two new FeOOH labeled bands appeared at 794 cm^{-1} and 683 cm^{-1} and (3633 cm^{-1} and 729.37 cm^{-1}) in nWTR and zeolite, respectively, indicating the role of iron oxyhydroxide on Cd adsorption process (Fig. 3b, c).

Adsorption kinetics

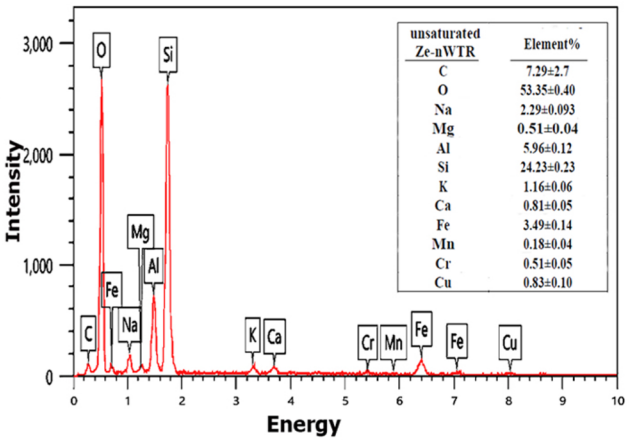
Understanding the kinetics and mechanisms of Cd adsorption reactions is a prerequisite for quantifying Cd sequestration by the studied adsorbents. A kinetic study was performed to estimate the equilibrium time. The Cd/zeolite or Ze-nWTR composite systems reached equilibrium within 2 h, while the nWTR-Cd system reached equilibrium after 8 h. These data are important because the equilibration time is a key parameter for the economics of wastewater treatment (Kadirvelu and Namasivayam, 2001). In addition, the amount of Cd adsorbed by the Ze-nWTR composite was higher than that of zeolite and nWTR (Fig. 4a). For all investigated adsorbents, Cd adsorption was very fast during the first 30 min. Cd was 99% adsorbed, followed by a slow adsorption step. Elkhatib et al. (2023) reported that the rapid adsorption of Cd is a surface phenomenon in which the pores on the adsorbent surface are rapidly filled in the initial stage, followed by slow diffusion and migration.

Kinetic modeling

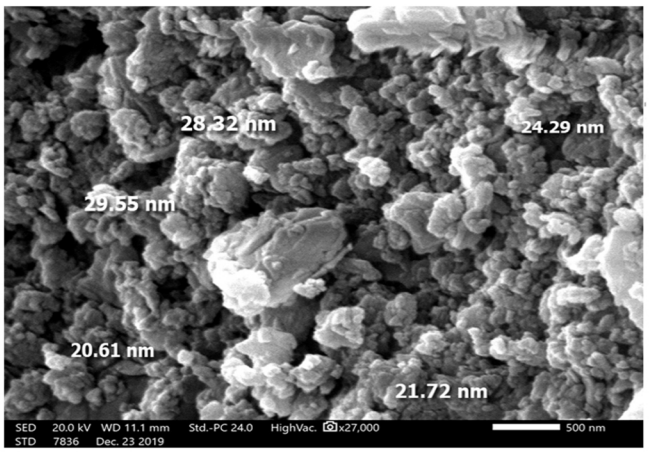
It is important to select a mathematical model that satisfactorily fits the data and provides a reasonable adsorption mechanism (Oualid and Mahdi 2007). The kinetic data of Cd(II) sorption by the three investigated adsorbents were

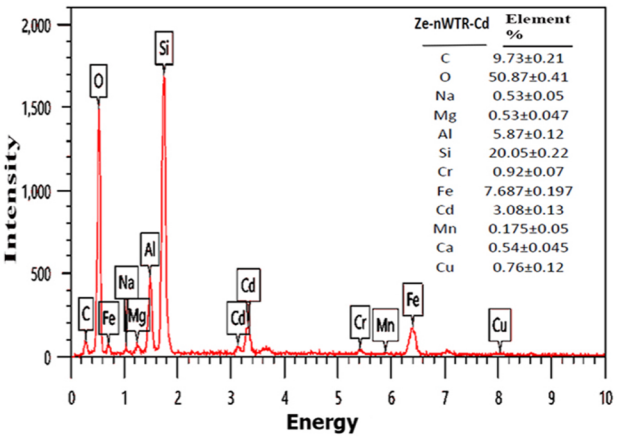

51.02 nm
51.02 nm
71.43 nm
25kV X20,000 1µm 090577

a

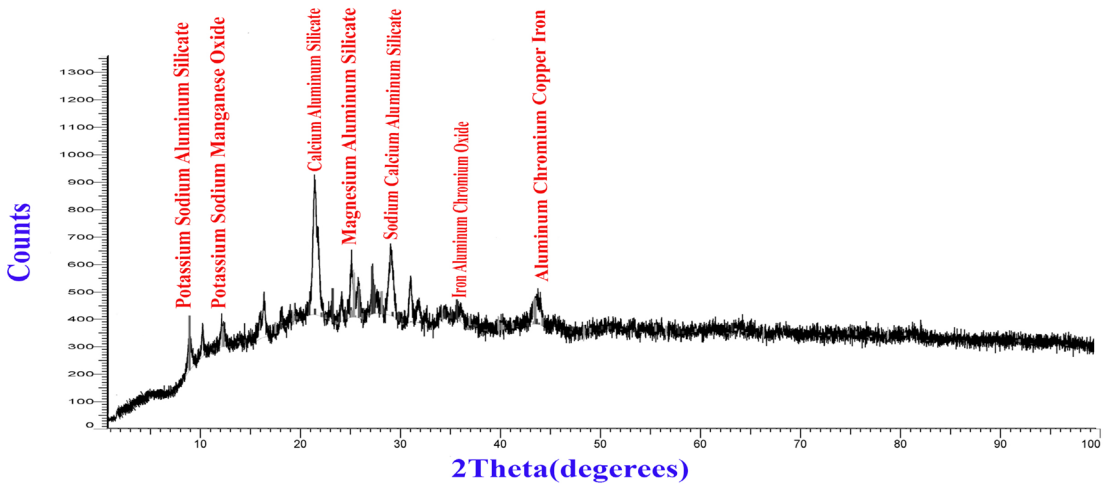

unsaturated Ze-nWTR
Element%
C 7.29±2.7
O 53.35±0.40
Na 2.29±0.093
Mg 0.51±0.04
Al 5.96±0.12
Si 24.23±0.23
K 1.16±0.06
Ca 0.81±0.05
Fe 3.49±0.14
Mn 0.18±0.04
Cr 0.51±0.05
Cu 0.83±0.10
Intensity
Energy

b


28.32 nm
24.29 nm
29.55 nm
20.61 nm
21.72 nm
SED 20.0 kV WD 11.1 mm Std.-PC 24.0 HighVac. x27,000
STD 7836 Dec. 23 2019
500 nm


Ze-nWTR-Cd
Element %
C 9.73±0.21
O 50.87±0.41
Na 0.53±0.05
Mg 0.53±0.047
Al 5.87±0.12
Si 20.05±0.22
Cr 0.92±0.07
Fe 7.687±0.197
Cd 3.08±0.13
Mn 0.175±0.05
Ca 0.54±0.045
Cu 0.76±0.12
Intensity
Energy

c


Potassium Sodium Aluminum Silicate
Potassium Sodium Manganese Oxide
Calcium Aluminum Silicate
Magnesium Aluminum Silicate
Sodium Calcium Aluminum Silicate
Iron Aluminum Chromium Oxide
Aluminum Chromium Copper Iron
Counts
2Theta(degerees)

◂**Fig. 2** Scanning electron microscopy (SEM) image and energy-dispersive X-ray (EDX) spectrum of nanocomposite (**a**) and Cd-saturated nanocomposite (**b**) and X-ray diffraction (XRD) analyses of nanocomposite (**c**)

analyzed using four kinetic models: first order (Elkhatib et al.1992), Elovich (Elkhatib et al. 1984), intraparticle diffusion (Elkhatib and Hearn 1988) and modified Freundlich (Hamadeen and Elkhatib 2022a, b). The model parameters, coefficient of determination (R^2) and standard error (SE) values for Cd retention of the studied adsorbents are presented in Table 1. The consistency between the experimental data and the values predicted by the model is expressed by the coefficient of determination (R^2) and the standard error (SE) of the estimated value. The model with the highest R^2 values (close to 1) and the lowest SE values was considered the best model that best represents the adsorption kinetics of Cd(II) (Fig. 4b). The R^2 and SE mentioned values belong to the average values of the three adsorbents. The adsorption rate (k_a) from the power function model was used to compare the Cd adsorption rates of the three investigated adsorbents. As shown in Table 1, ka appeared in the order of nanocomposite (49,306.03 min^{-1}) > nWTR (46,902.93 min^{-1}) > zeolite (45,729.87 min^{-1}).

Adsorption isotherm

Figure 5a shows the Cd(II) adsorption isotherms by nWTR, zeolite and Ze-nWTR composite. A continuous increase in the amount of Cd adsorbed by the three studied adsorbents was observed with the increase of Cd concentration from 40 to 640 mg L^{-1}. The Cd adsorption capacity of the three adsorbents studied was in the following order: nanocomposite (Ze-nWTR) > nWTR > Zeolite). Interestingly, the shapes of the Ze-nWTR composite and nWTR sorption isotherms are L-shaped isotherms according to the Giles classification (Giles et al. 1974), indicating an initial slope that does not increase with increasing pollutant concentration. The shape of the Cd adsorption isotherm by zeolite is an S-type isotherm, which is characterized by an increase in the slope as the pollutant concentration increases.

The adsorption equilibrium model

Cd adsorption parameters for three adsorbents (nWTR, zeolite and Ze-nWTR nanocomposites) studied using seven adsorption isotherm models (Langmuir, Freundlich, Elovich, Temkin, Fowler–Guggenheim (F.G.), Kiselev and Hill de Boer) were used for data interpretation (Table 2). When describing the adsorption data, R^2 and SE values (Table 2) were used to determine the best fit for the isotherm. The R^2 and SE values of the studied models (Table 2 and Fig. 5b) indicate that the Langmuir model is the most successful model in describing the Cd adsorption data. Therefore, it is assumed that the removal of Cd from the surface of the three investigated adsorbents is a monolayer adsorption process. The maximum adsorption capacity (q_{max}) of Ze-nWTR (147.9 mgg^{-1}) was 3 and 5.9 times higher than the q_{max} values of nWTR and zeolitic adsorbent, respectively (Table 2). The zeolite coating process using nWTR and the synergistic action between clay and iron nanoparticles are responsible for the high adsorption capacity of the nanocomposite (Hamadeen et al. 2022). Therefore, it is recommended to use the Ze-nWTR nanocomposite as an effective adsorbent for the removal of Cd from polluted water sources (Arancibia-Miranda et al. 2016).

Operating conditions for Cd removal

Effect of solution pH and temperature

The Cd sorption process was monitored over a solution pH range of 4–9, adsorbent dose of 0.2 g and three different temperatures (287,297,307 K). Figure 6 shows that Cd removal increases with increasing solution pH and peaks at pH 9. The influence of different pH on the Cd ion removal rate of the studied adsorbents can be explained by the surface charge characteristics of the adsorbents and the ionization state of Cd (Mittal 2006). Therefore, the zero point charge (pHzpc) of the nanocomposite was determined to be 7.2 (Fig. S3). In solutions with a pH greater than 7.2, the repulsion between positively charged Cd and the surface charge of nanoparticles is minimized, resulting in increased Cd adsorption (Elkhatib et al. 2016). Additionally, the Langmuir adsorption capacity of the nanocomposites increased from 147.9 to 270 mgg^{-1} as the temperature increased from 279 to 308 K(Al-Qodah et al. (2007) reported that the adsorbate diffusion rate in the internal pores of adsorbent particles increases with increasing temperature.

The effect of competing cations

Industrial wastewater contains many metal ions that can interact with adsorbents and compete for binding sites. Therefore, it is important to study the competition between heavy metals for Cd adsorption by Ze-nWTR. To evaluate the proportion of Cd adsorbed by Ze-nWTR in single and multi-element systems, a series of adsorption studies were performed in the presence and absence of Zn, Cu and Ni at different Cd concentrations (20, 60,180 mg L^{-1}). As shown in Fig. 7a, the presence of Zn^{2+},Cu^{2+},Ni^{+2} cations reduced the removal of Cd ions from solution by the Ze-nWTR nanocomposite because of the antagonism between the charged

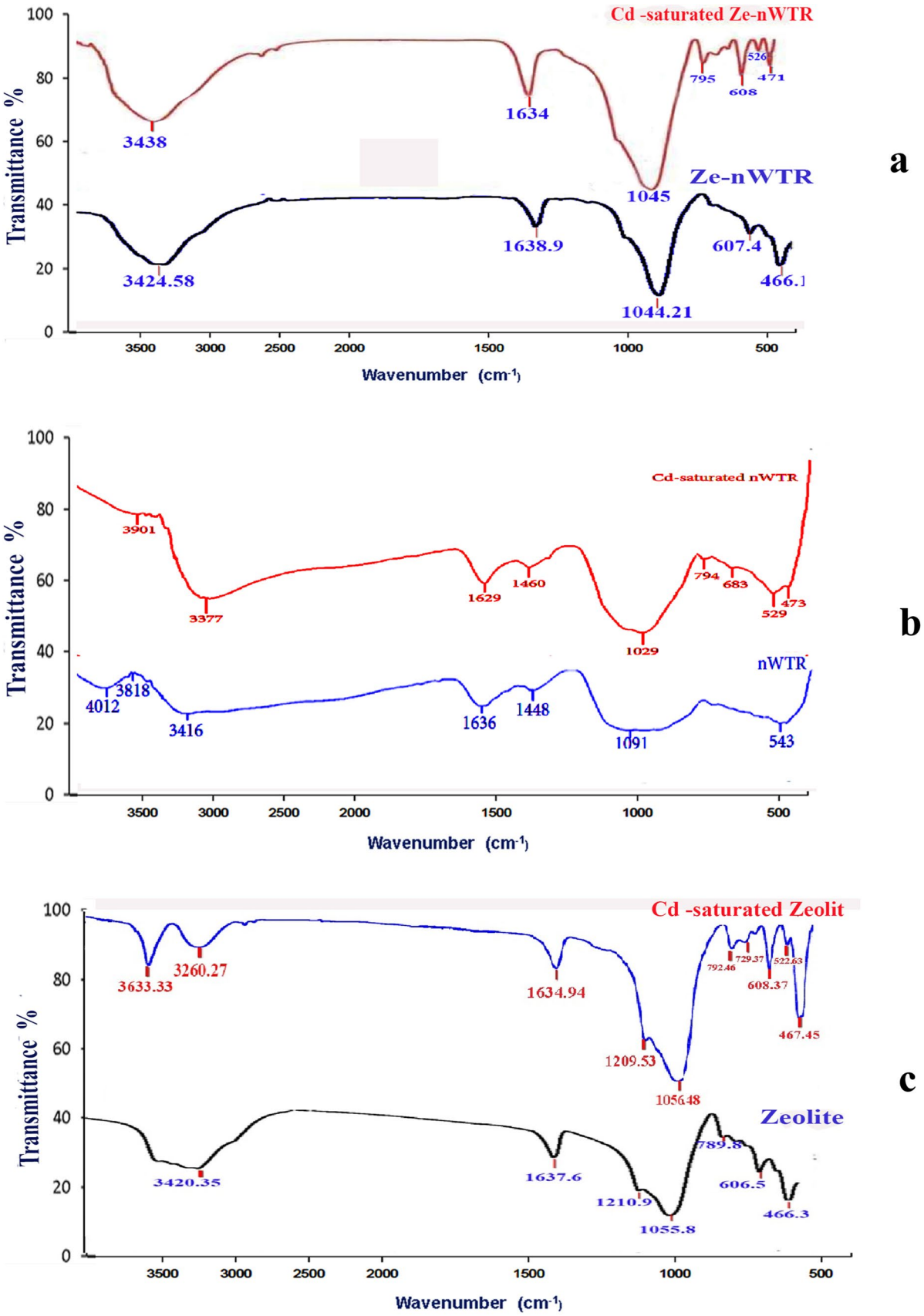


Fig. 3 FTIR spectra of Ze-nWTR (**a**), nWTR (**b**) and zeolite (**c**) before and after Cd(II) adsorption

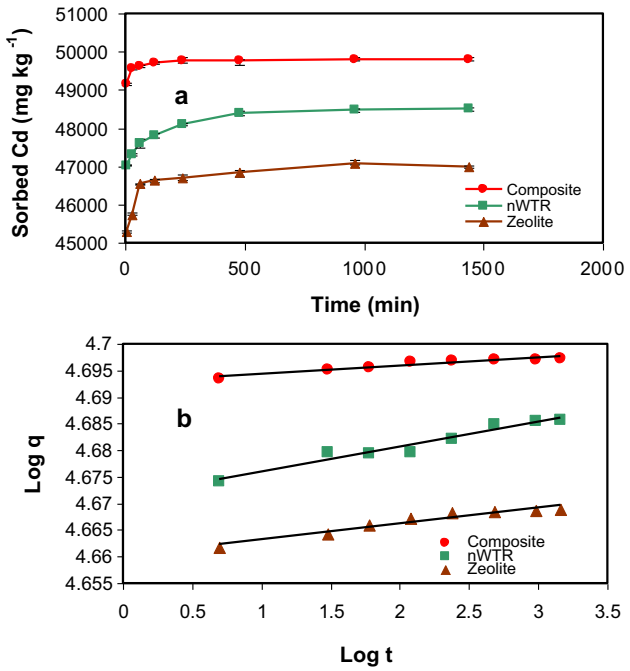


Fig. 4 Kinetic of Cd sorption by nWTR, zeolite and nanocomposite (Ze-nWTR) (**a**) and power function model for Cd sorption by the three sorbents (**b**). Initial Cd concentration is 500 mgL^{-1}

metal for the available sorption sites on Ze-nWTR nanocomposite surface and the increase in ionic strength of the solution (Hezarjaribi et al. 2021; Liu Y et al. 2020).

Effect of sorbent dose

The capacity of an adsorbent for a given initial concentration is highly dependent on the capacity of the adsorbent. The effect of Ze-nWTR nanocomposite, nWTR and zeolite bulk on Cd(II) removal from aqueous solution was determined by adding different doses (0.1–0.3 g) of each adsorbent using 20 mL of 500 mg Cd L^{-1}. Focus once every 60 min. Figure 7b shows the effect of adsorbent weight on Cd removal. The results show that there is a significant difference in the adsorption capacity of Cd between different doses. For example, by increasing the dosage of Ze-nW nanocomposite, the removal rate of Cd increased from 33,225 to 91,310 mg/kg. For a given Cd^{2+} concentration, increasing the adsorbent weight increases the surface area and the number of active sites available for Cd interaction.

Effect of temperature

Thermodynamic parameters for Cd retention in Ze-nWTR nanocomposites were calculated at different initial Cd concentrations (100, 250, 500 and 1000 mgL^{-1}) and different pH values (4,7,9) to determine adsorption nature (Al-Anber 2011). At initial concentration (100 mg L^{-1}) and pH 9, standard free energy changes ($\Delta G°$) for Cd(II) sorption were observed by Ze-nWTR to be − 22.302, − 27.252 and − 32.455 kJ mol^{-1} at 14 °C, 24 °C and 34 °C, respectively (Table 3). The negative values of $\Delta G°$ indicate the feasibility of the Cd adsorption process and explain the

Table 1 Kinetics model constants and determination coefficients and standard error of estimate for cadmium adsorption by three different sorbents

Models	Parameter	nWTR	Zeolite	Composite
Elovich $q_t = (1/\beta)\ln(\alpha\beta) + (1/\beta)\ln t$	α (mg g^{-1} min^{-1})	$4.730E^{+9}$	$9.77E^{+142}$	$7.999E^{+206}$
	β (mg g^{-1})	0.0044	0.0065	0.0095
	R^2	0.95	0.6041	0.83
	SE	774.31	253.56	97.52
First order $\ln(q_0 - q) = a - k_a t$	K_d (min^{-1})	0.004	0.004	0.371
	a (μg g^{-1})	6.861	5.8	278.7
	R^2	0.971	0.718	0.317
	SE	0.247	1.036	0.793
Parabolic diffusion $q = a + k_a t^{1/2}$	K_d (μgg^{-1} $min^{-1/2}$)	31.425	18.240	12.188
	a (μg g^{-1})	47,493	46,110	49,445
	R^2	0.827	0.387	0.497
	SE	741.92	375.33	168.34
Power function $q = k_a C_0 t^{1/m}$	K_a (min^{-1})	46,902.93	45,729.87	49,306.03
	$1/m$	0.0047	0.003	0.0015
	R^2	0.953	0.937	0.920
	SE	0.0009	0.002	0.0009

q or q_t = Cd adsorbed (mg kg^{-1}) at time t, q_0 = Cd adsorbed (mg kg^{-1}) at equilibrium, k_a = apparent sorption rate coefficient, α = the initial adsorption rate (mg g^{-1} min^{-1}), β = a constant related to the extent of surface coverage (mg g^{-1}), a = a constant; k_d = apparent diffusion rate coefficient, q = adsorbed Cd (mg kg^{-1}), C_0 = initial Cd concentration (mg L^{-1}), t = reaction time (min), k_a = sorption rate coefficient (min^{-1}), and $1/m$ = constant. R_2 = determination coefficient, SE = standard error of estimate

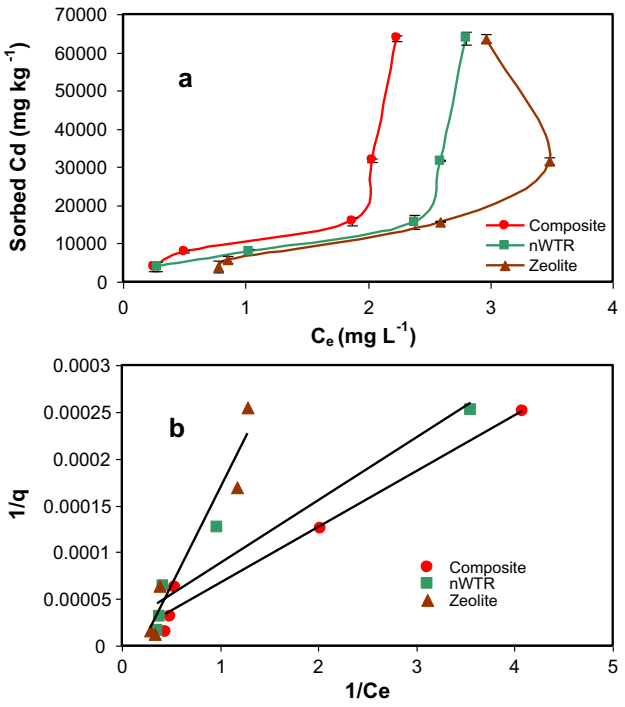


Fig. 5 Cadmium sorption isotherms for nWTR, zeolite and nanocomposite (Ze-nWTR) (**a**) and Langmuir isotherms model for the three sorbents (**b**)

spontaneous response of Cd on Ze-nWTR nanocomposite adsorbents (Bayuo 2021). As shown in Fig. 8 and Table 3, a decrease in the $\Delta G°$ value (i.e., an increase in negativity) means that the amount of adsorption increases with increasing temperature. This result is consistent with the results of Fawzy et al. (2022), who found a decrease in $\Delta G°$ with increasing temperature for the biosorption of Cd on alginate-immobilized *T. ornata* biomasses. In addition, the $\Delta G°$ value increased negatively with increasing pH value, indicating that there were more adsorption sites as the pH value increased from 4 to 9 (Qadeer 2005; Chen and Wang 2006). In contrast, $\Delta H°$ values were positive at different initial solution concentrations, indicating the endothermic nature of Cd adsorption by Ze-nWTR (Suresh et al. 2010) (Table 3). The data in Table 4 showed that the $\Delta H°$ value decreases with the increase of the initial concentration, which means that less energy is required for the Cd adsorption reaction in Ze-nWTR due to the increase of the initial Cd concentration. Typically, $\Delta H°$ between 2.1 and 20.9 kJ mol $^{-1}$ indicate physical adsorption, while values between 20.9 and 408 kJ mol $^{-1}$ confirm chemisorption. (Tuzen et al. 2009). Therefore, physical and chemical attractions between Cd and Ze-nWTR are suggested due to the different large values of $\Delta H°$ (123,292–18,600 J mol^{-1}) for Cd adsorption on Ze-nWTR at different initial solution concentrations. The negative values of $\Delta S°$ indicate that the dissociation mechanism is involved in the Cd(II) adsorption process (Suresh et al. 2010).

Cd adsorption mechanism

The Cd adsorption mechanism of Ze-nWTR nanocomposites was revealed by FTIR, XRD and EDX analyses. The XRD pattern confirmed the sorption reaction of Cd on the nanocomposite evidenced by cadmium peak (3.08%) detected in Cd-loaded Ze-nWTR nanocomposite (Fig. 2b). The FTIR analysis of zeolite showed that the band at 3420 cm^{-1} (OH bending vibration) completely disappeared after Cd was trapped on the zeolite surface, indicating the role of the OH functional group in Cd adsorption. Due to the presence of OH groups, cadmium can form surface complexes with the outer sphere zeolite surface (Peng et al. 2021; Ma et al. 2022). Therefore, ion exchange between H and Cd^{2+}, which corresponds to the OH group of the zeolite, is the proposed adsorption mechanism, as shown in the following equation:

$$HO{-}Ze{-}OH + Cd^{2+} = HO{-}Ze{-}O{-}Cd + 2H^{+}$$

For the nWTR adsorbent, the FTIR spectrum of nWTR after Cd adsorption shows that the band associated with the O–H bending vibration at 4012 cm^{-1} has completely disappeared. Increasing intensities and changing the location of O–H bending vibrations band from 3416 to 3377 cm^{-1}, the H_2O bending vibrations band from 1636 to 1629 cm^{-1}, the FeOH modes of peroxygite bending vibration from 1091 to 1029 cm^{-1} are identified. Moreover, the shift and enhancement of the two bands at 794 cm^{-1} and 683 cm^{-1} compared to FeOOH are a clear indication of real molecular interactions. Therefore, the six-coordinate structure of Cd suggests that it can form a bidentate complex on the surface of FeOOH and the inner sphere of nWTR, as shown in Fig. 9. It is also noteworthy that the Ca ratio decreased from 7.8 to 4.2% after Cd-saturated nWTR according to EDX analysis, as shown in Fig. (S2) (Supplementary Material). This result indicates the ability of Cd to replace Ca inside the octahedral FeOOH structure of nWTR, which can be attributed to the partial similarity between the ionic radii of Cd^{2+} (0.97 Å) and Ca^{2+} (0.99 Å) (Ji et al. 2020). Therefore, the general predicted mechanism of Cd adsorption in Ze-nWTR nanocomposites is initially through the electrostatic attraction between Cd ions in solution and zeolite OH. Subsequently, the adsorbed Cd can be specifically adsorbed on FeOOH-nWTR by inner-sphere complexation. Additional reactions may occur due to Cd occlusion of the internal FeOOH structure.

Table 2 Equilibrium model constants and determination coefficients and standard error of estimate for cadmium adsorption by three different sorbents

Models	Parameter	nWTR	Zeolite	Nanocomposite
Freundlich $q_e = K_F C_e^{1/n}$	K_F (mL g^{-1})	11,475	7194.701	15,796
	$1/n$	1.004	1.3669	1.007
	R^2	0.796	0.8006	0.845
	SE	0.572	0.568	0.499
Langmuir $q_e = q_{max}(K_L C_e/1 + K_L C_e)$	q_{max} (µg g^{-1})	50,000	25,000	147,857
	K_L (L mg^{-1})	0.28571	0.15	0.117
	R^2	0.919	0.937	0.974
	SE	0.00003	0.00005	0.00002
Elovich $q_e/q_m = K_E C_e \exp(-q_e/q_m)$	q_{max} (µg g^{-1})	100,000	50,000	100,000
	K_E (L mg − 1)	1.08	1.11	1.13
	R^2	0.516	0.817	0.440
	SE	0.398	0.276	0.373
Temkin $\theta = RT/\Delta Q \ln K_0 C_e$	ΔQ (kJ mol^{-1})	7.251	3.376	19.779
	K_0 (L g^{-1})	3.065	1.537	3.947
	R^2	0.47	0.525	0.5422
	SE	0.409	0.580	0.133
Fowler–Guggenheim (FG) $K_{FG} C_e = \theta/1 - \theta \exp(2\theta w/RT)$	W(kJ mol^{-1})	−2.2445	−2.132	−3.7482
	K_{FG} (L mg^{-1})	0.17028	0.0189	0.080
	R^2	0.5482	0.9165	0.705
	SE	0.496	0.321	0.385
Kiselev $k_1 C_e = \theta/(1-\theta)(1 + k_n\theta)$	k_1 (L mg^{-1})	0.3491	0.0832	0.109
	kn	1.80751	25.0381	1.305
	R^2	0.8239	0.0137	0.95
	SE	0.895	2.642	0.398
Hill–deBoer $K_1 C_e = \theta/(1-\theta) \exp(\theta/(1-\theta) - K_2\theta/RT)$	K_1 (Lmg^{-1})	7.811	6.6	13.16
	K_2 (kJ mol^{-1})	12.03	18.79	12.13
	R^2	0.824	0.876	0.84
	SE	0.675	4.60	0.421

qe(mg g^{-1}) = Cd adsorbed per gram of adsorbent, Ce (mg L^{-1}) = equilibrium Cd concentration in solution, K_F = a constant related to adsorption capacity of the adsorbent (mL g^{-1}), n = a constant, q_{max} (mg g^{-1}) is the maximum adsorption capacity of the adsorbent, KL (L mg^{-1}) = Langmuir constant related to the free energy of adsorption, θ = fractional coverage, R = the universal gas constant (kJ mol^{-1} K^{-1}), T = the temperature (K), $\Delta Q = (-\Delta H)$ the variation of adsorption energy (kJ mol^{-1}), and K_0 = Temkin constant (L mg^{-1}), K_{FG} = Fowler–Guggenheim constant (L mg^{-1}), w = the interaction energy between adsorbed molecules (kJ mol^{-1}), k_1 = Kiselev constant (L mg^{-1}), k_n = a constant of complex formation between adsorbed molecules, K_1 = Hill–de Boer constant (L mg^{-1}), and K_2 (kJ mol^{-1}) = a constant related to the interaction between adsorbed molecules. A positive K_2 means attraction between adsorbed species and a negative value means repulsion

Reusability

The regeneration of the functional groups of the nanocomposites used by frequent movements corresponds to their stability, which is very important for industrial wastewater treatment. Therefore, the reusability and stability of Ze-nWTR nanocomposites were investigated for six consecutive adsorption/desorption cycles using 0.01 M HCl solution to desorb loaded Cd(II). The cumulative Cd absorbed by Ze-nWTR nanocomposites at initial Cd concentrations of 10.0 mg L^{-1} and/or 100.0 mg L^{-1} are shown in Fig. 10.The adsorption efficiency of Ze-nWTR nanocomposites for Cd(II) decreased by 1.7%, 1.9%, 3.6% and 3.7% during the second, third, fifth and, the sixth cycle, respectively. The results showed that the Ze-nWTR nanocomposite could be efficiently reused for up to six adsorption cycles with little change in the adsorbed Cd, indicating the high stability of the nanocomposite-loaded Cd. This makes the sorption process economical, reliable and technically attractive due to the low generation of solid waste.

Cadmium removal efficiency of nanocomposites

Batch study

The efficiency of nanocomposites for Cd(II) removal was investigated using batch experiments on real wastewater.

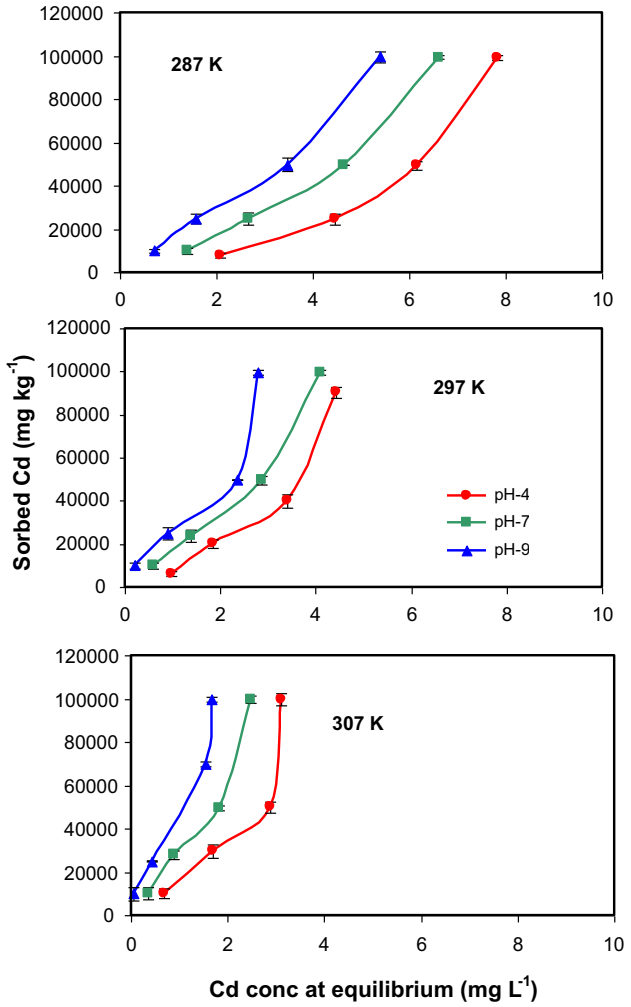


Fig. 6 Effect of pH on Cd sorption by nanocomposite (Ze-nWTR) at different temperature (287, 297, and 307 K)

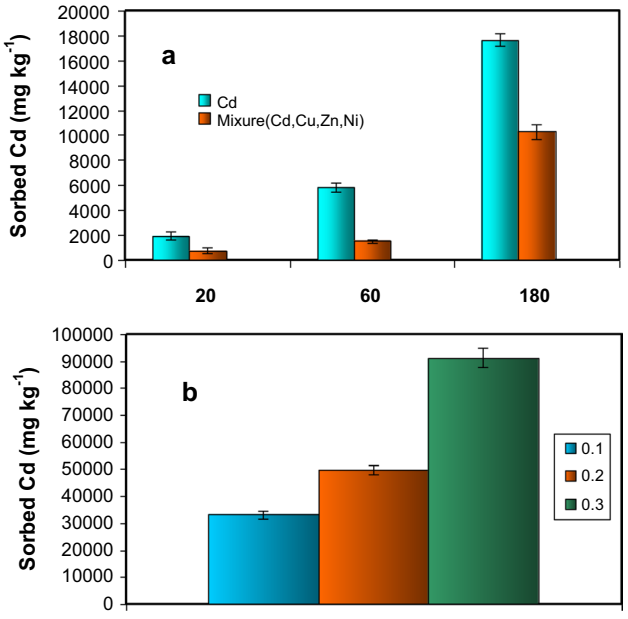


Fig. 7 Effect of competitive cations (Ni, Zn, Cu) at different Cd concentrations (20, 60,180 mgL^{-1}) (**a**), and sorbent dose (0.1, 0.2, 0.3 g) (**b**) on Cd sorption by nanocomposite (Ze-nWTR)

Cd-contaminated industrial wastewater from the Rakta paper mill was treated with Ze-nWTR to remove Cd. The results showed that Ze-nWTR successfully removed 98.45% of Cd from Cd-contaminated industrial wastewater. Batch experiments showed that the Cd removal potential of Ze-nWTR was not affected by the presence of different anions (e.g., SO_4, CO_3, HCO_3, Cl-) in industrial wastewater. In addition, the nanocomposite removed 97.53% of cadmium (Cd) from Al-Bilali agricultural drainage. These results demonstrate the suitability and efficiency of Ze-nWTR for Cd removal from real wastewater.

Column research

Using a bed reactor under continuous flow conditions (flow rate 3 mL min^{-1}) by Ze-nWTR nanocomposites, the Cd removal efficiency reached 95.5% and 98% for agricultural drainage and industrial discharge, respectively. The highest removal rate of the Ze-nWTR nanocomposite indicates that the nanocomposite can be used as a potential adsorbent for the removal of various toxic pollutants from industrial and agricultural wastewater. Overall, the results of this study showed that the Ze-nWTR nanocomposite is a very environmentally friendly and reusable adsorbent for the effective removal of Cd from wastewater.

Comparison of various adsorbents for Cd removal

The effective removal of Cd(II) from wastewater by the Ze-nWTR nanocomposites was further evaluated by comparing the q_{max} values with the adsorbents shown in Table 4. Clearly, Ze-nWTR nanocomposites have higher Cd(II) adsorption capacity compared to other nano-adsorbents such as SiO2@DOPP nanocomposites, plant magnetic nanoparticles, hydroxyapatite coated zinc ferrite nanocomposites, gum iron modified oxide, and sodium-exchanged montmorillonite (Saravanan et al. 2012; Bunhu et al. 2017; Ali et al. 2019; Das and Dhar 2020; Saini et al. 2021). These results confirmed that the Ze-nWTR nanocomposite performed better than the aforementioned nanocomposites in removing Cd(II) from wastewater.

Table 3 Thermodynamic parameters for Cd adsorption by nanocomposite (Ze-nWTR) sorbent at different solution pH values (4–9) and 4 initial Cd concentrations

Initial concentration (mg l^{-1})	pH	T (K)	ΔG° (J mol^{-1})	ΔS° (Jmol^{-1} K^{-1})	ΔH° (J mol^{-1})
100	4	287	− 19,206	− 430.65	104,787
		297	− 22,320		
		307	− 27,819		
	7	287	− 21,835	− 447.06	107,208
		297	− 24,098		
		307	− 30,777		
	9	287	− 22,302	− 507.15	123,292
		297	− 27,252		
		307	− 32,445		
250	4	287	− 20,493	− 162.02	26,187
		297	− 21,576		
		307	− 23,733		
	7	287	− 22,326	− 209.94	37,866
		297	− 24,608		
		307	− 26,525		
	9	287	− 22,737	− 439.64	103,935
		297	− 25,643		
		307	− 31,530		
500	4	287	− 21,385	− 151.25	22,063
		297	− 22,778		
		307	− 24,410		
	7	287	− 23,469	− 185.97	30,083
		297	− 24,791		
		307	− 27,188		
	9	287	− 25,522	− 240.82	43,866
		297	− 27,110		
		307	− 30,339		
1000	4	287	− 22,308	− 142.69	18,600
		297	− 23,868		
		307	− 25,162		
	7	287	− 23,871	− 164.54	23,574
		297	− 24,855		
		307	− 271,612		
	9	287	− 24,396	− 215.76	37,851
		297	− 25,579		
		307	− 28,711		

Conclusion

Ze-nWTR nanocomposites were prepared by the grinding method. Subsequently, SEM–EDX, XRD and FTIR analyzes were used to study the nanocomposites. The spherical nWTR nanoparticles distributed on the zeolite surface of the film are clearly visible in the size range of 51.02–71.43 nm. The synergistic behavior between zeolitic clay and iron-nWTR nanoparticles was evident as the maximum value of adsorption capacity (q_{max}) of the nanocomposite (147.9 mg g^{-1}) was 3 and 5.9 times higher than that of nWTR and zeolite, respectively, at 287 K. In addition, the adsorption rate (k_a) from the power function model was higher for nanocomposite (49,306.03 min^{-1}) than for nWTR (46,902.93 min^{-1}) and zeolite (45,729.87 min^{-1}). The optimal conditions for Cd removal by nanocomposites are pH 9 and 307 K. The suggested mechanism of the Cd adsorption in the nanocomposite is started by the traction of static electricity between the Cd and the OH-zeolite, and then fixed into FeOOH-nWTRs internal surface. A slight change in the Cd adsorbed on the nanocomposite was observed as a result of the high stability of the nanocomposite loaded with Cd. In addition, Cd removal from agricultural drainage and industrial discharge are

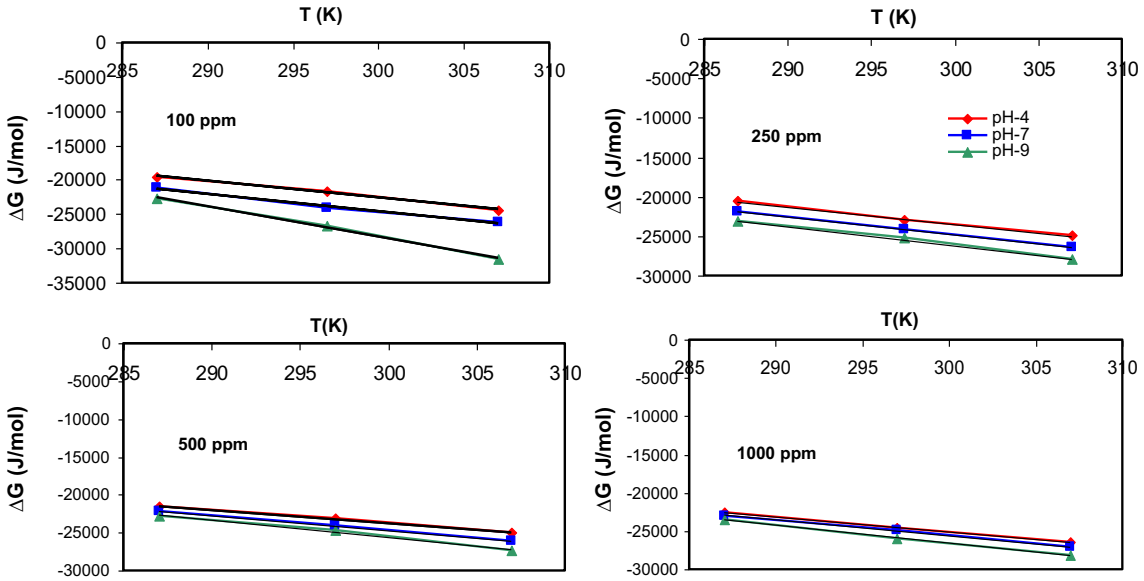


Fig. 8 Arrhenius plot of Cd adsorption on nanocomposite(nMgO and Bentonite) (T = 287, 297, and 307 K; pH = 4, 7, and 9; Cd concentrations = 100, 250, 500 and 1000 mgl^{-1})

Table 4 Maximum adsorption capacities (q_m) of Cd(II) adsorption onto nanocomposite and various adsorbents listed in the literature

Adsorbent	q_{max} mgg^{-1}	References
Ze-nWTR	147	Current study
SiO_2@DOPP Nanocomposite	142	Saini et al. (2021)
nanoscale magnesia	16.54	Koju et al. (2017)
Oil palm residual biomass/Al_2O_3 nanoparticles composite	17.4	Herrera-Barros et al. (2020)
Phytogenic magnetic nanoparticles	68.41	Ali et al. (2019)
Hydroxyapatite Encapsulated Zinc ferrite) nanocomposites	120.33	Das and Dhar (2020)
Gum kondagogu modified iron oxide NPs	106.8	Saravanan et al. (2012)
Shellac coated iron oxide NPs	18.80	Gong et al. (2012)
Sodium-exchanged montmorillonite nanoclay	18.73	Bunhu et al. (2017)

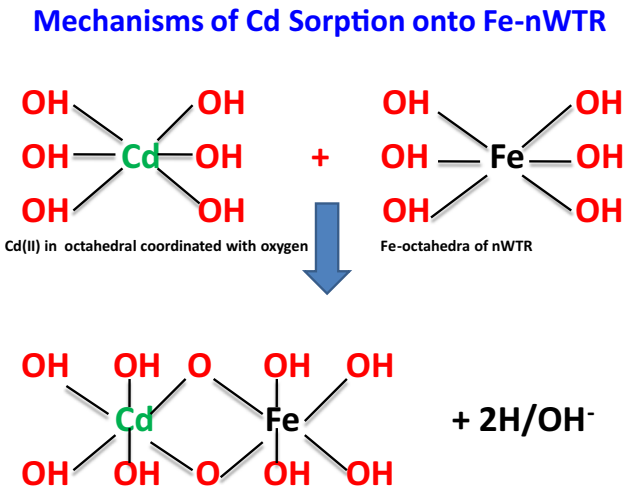


Fig. 9 Schematic diagram of surface complexation of cadmium onto Fe-nWTR

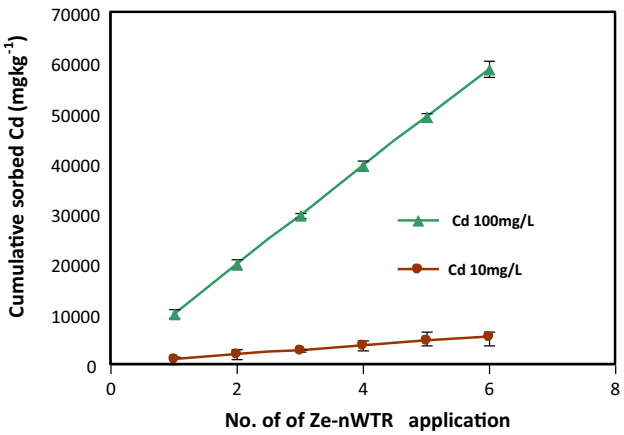


Fig. 10 Effect of repetitive application of nanocomposite on cumulative sorbed Cd at initial Cd concentration 10 and 100 mg l^{-1}

efficiently emitted at 95% and 98%, respectively. The final results confirmed the effectiveness, reusability and sustainability Ze-nWTR nanocomposite in removing Cd from contaminated industrial wastewater.

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Author contributions EAE contributed to concept, supervising investigation, and writing and editing. MLM involved in analysis, data validation, and writing and editing. AFS involved in supervising investigation and writing. SA involved in methodology, analysis and writing. All authors reviewed the manuscript.

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Data availability All data generated or analyzed during this study are included in this published article and its supplementary information files.

Declarations

Conflict of interest The authors have no competing financial or personal interests.

Ethical approval Not applicable.

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