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Binary adsorption of toxic nickel(II) and cadmium(II) ions from aqueous solution by acid modified chilli peppers

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ABSTRACT

The acid-modified chilli peppers, a novel adsorbent, were prepared and used to absorb Ni(II) and Cd(II) ions from aqueous solution. Batch experiments with raw chilli peppers were compared with those of acid-modified chilli peppers. Batch experiments were conducted to evaluate the adsorption capacities of both sorbents under different conditions, including pH, concentration, contact time and temperature, in solutions. Bands with oxygen groups (-OH, -COOH, -C = O, -COC and -CO) on both sorbents were identified by Fourier transform infrared spectroscopy. Scanning electron micrographs of raw chilli peppers showed a morphology resembling spheres, while acid-modified chilli peppers showed a structure resembling a mesh of a mixture of different shapes, including squares and triangles. Maximum sorption capacities were achieved at pH 7, with the uptake of Ni(II) and Cd(II) ions dependent on pH.

The highest adsorption capacities for raw chilli peppers and acid-modified chilli peppers were observed at 70 °C. The sorption capacities increased with increasing temperature. The concentration effect showed that as the concentration of Ni(II) and Cd(II) ions increased on raw chilli peppers and acid-modified chilli peppers, the adsorption capacity also increased. On raw chilli peppers, the rate of removal of Ni(II) and Cd(II) ions in solution was 60 min, while on acid-modified chilli peppers it took 80 min. The adsorption of Ni(II) and Cd(II) ions was best described by the Freundlich model with heterogeneous coverage and maximum capacities of 45.33 and 39.12 mg/g, respectively. The uptake of Ni(II) and Cd(II) ions was endothermic and showed positive values (ΔH^o). Gibb's free energy (ΔG^o) for Cd(II) and Ni(II) ions on the activated carbon showed that the reaction was spontaneous. The change in entropy (ΔS^o) of the reactions showed positive magnitudes for both pollutants, indicating a high degree of randomness in the solid-liquid phase. The kinetic model that best fitted the mechanism was pseudo-first order for Ni(II) and Cd(II) ions, indicating correlation numbers of R^2 values of 0.9923–0.9995. Therefore, the acid-modified chilli peppers can be used as a viable alternative adsorbent for effective removal of Cd(II) and Ni(II) ions from aqueous solution.

1. Introduction

Human society faces a great challenge due to environmental pollution [1]. Environmental pollution and contamination by toxic metals cause significant threats to human health and the environment [2]. Toxic metals have polluted the environment due to rapid urbanisation and industrialisation, which has also accelerated the rate at which these metals are transported through the ecosystem [3]. In recent years, toxic metal pollution has become a major global problem [1]. The rapid growth of sectors such as fertilisers, textiles, tanneries, batteries, paper, jewellery, pulp and others has resulted in the direct or indirect release of effluents containing toxic metals into the environment [4–6]. The presence of toxic metals in the environment is considered a significant health risk to human health. Toxic metals do not decompose and can enter the food chain via various routes and accumulate toxically in living organisms. Long-term effects of low-level chronic toxicity of toxic metals, such as liver and lung damage, bone deterioration and even blood damage, can be harmful [5,6].

Most ions of nickel and cadmium are found in soils and water [7]. Cadmium leakage to water bodies and the environment is influenced by industrial processes such as smelting, alloy manufacturing, and pesticide use [4]. Cadmium poisoning of water systems also occurs from improper

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disposal of leftover paint, fertilizer, and Ni/Cd batteries [8]. The nickel industry subsequently uses nickel primarily for stainless steel, and carcinogenic nickel refinery dust and nickel subsulfide (Ni_3S_2) are easily found as small particles in water bodies [8]. Although nickel is thought to be safe when taken as directed and is necessary for human health to function, exposure to excessive amounts, even at low concentrations, can have a fatal effect on health [9]. Among the health effects of nickel are respiratory systems, severe inflammation of the nasal membranes, hypersensitivity, including bronchial asthma, and contact dermatitis. As a result, acute effects in humans include nausea, dizziness, and chest pain [10]. Nickel toxicity also causes weight loss, hepatic and renal damage, poisoning of the cardiovascular system, skin irritation, sensitization, and stimulation of neoplastic transformation [11]. Cadmium is a toxic, non-essential toxic metal that interacts with DNA repair processes [7]. It has negative effects on oxidative stress, plant nutritional deficiencies, and cellular enzyme systems. In addition to causing cancer and bone disease, cadmium ions can have an impact on important organs like the brain, kidneys, heart, and lungs [4]. Furthermore, because cadmium and zinc have the same oxidation state, cadmium can replace zinc in metallothionein, preventing zinc from serving as a free radical scavenger in cells. Tubular dysfunction may arise from the formation of a cadmium metallothionine complex due to this displacement [11].

Traditional methods for the detection of Cd(II) and Ni(II) include high-performance liquid chromatography, atomic absorption spectrometry and inductively coupled plasma mass spectrometry and others [12]. Other technologies include ion exchange, reverse osmosis, chemical precipitation, electrochemical processes, and adsorption [13–15]. However, these methods are not suitable options due to their low removal efficiency and high operating costs [12,16]. Therefore, it is important to develop a sensitive, practical and cost-effective method for the detection of Cd(II) and Ni(II). Adsorption is considered to be one of the most commonly used methods for the uptake of metal ions due to its ease of use, cost efficiency advantages and recovery [17]. Therefore, the detection of Cd(II) and Ni(II) with a very simple method that is fast and inexpensive is of utmost importance. In general, the sorption capacity of raw materials is limited [18]. To solve this problem, modification methods are usually used to increase the sorption capacity of adsorbents for toxic metals [19]. Under appropriate conditions, the surface of the adsorbent can be treated with chemical methods to increase the content of functional groups on the surface so that it can form more adsorption sites during the uptake process, thereby improving its sorption capacity for toxic metals [20]. Strongly to slightly oxidising substances such as hydrochloric acid (HCl), nitric acid (HNO_3), phosphoric acid (H_3PO_4), potassium permanganate ($KMnO_4$) and sulphuric acid (H_2SO_4) have been shown to increase the oxygen-containing functional groups such as carboxyl (-COOH) and carbonyl (-C = O) on the surface of the material, which ultimately improves the sorption capacity of the material [21].

Many types of materials have been developed and used to remove toxic metals from wastewater, including activated carbon, chitosan and cellulose [21]. However, these materials have the disadvantage of being very economical and mechanically unstable [22]. Plant materials and other agricultural biosorbents have been used for toxic metal removal studies due to their abundant availability, lignocellulosic nature with significant porosity, presence of various functional components and reusability [23]. However, in order to use these materials for the removal of toxic metals from wastewater, they need to be pretreated to some extent to expose the binding sites [24]. Therefore, various chemicals such as acids, ethanol, alkalis, organic acids and acetone are usually used for the pretreatment of biosorbents [24]. By chemically modifying the biosorbents, it is possible to introduce counterions or change the functional groups so that the metal ions can attach to the surfaces of the sorbents in solution [23]. In many cases, an acidic pre-treatment proves to be more effective, as impurities and ions that could block the binding sites can be easily removed [24].

Among the low-cost biosorbents, chilli pepper, also known as *Capsicum annuum*, is the most widely available agricultural material. Chilli is widely cultivated and used for food and spice purposes. Chilli peppers were used as a potential absorbent in this study because they are abundant in nature, environmentally friendly, accessible, inexpensive, reusable, non-selective to pollutants, easy to produce, and their surface has several functional groups such as carboxyl and hydroxyl [25]. These properties make the chilli pepper an advantageous material for adsorption technology. Although several researchers have used chilli pepper as an adsorbent for the removal of various pollutants, only a few studies have been conducted using chilli for the removal of metal ions. Some of these studies include the investigation of the removal of Pb(II) and Cd(II) ions in binary and simple form using chilli pepper seeds from aqueous solutions [25], the characterisation of activated carbon with different concentrations of sodium hydroxide [26] and the synthesis of biochar from chilli seeds and its application for the removal of ibuprofen from water [27]. Marfil Parra et al. (2020) [28] investigated the morphology and structure of raw chilli and Aziz et al. (2021) [29] used chilli stems as an adsorbent to remove methylene blue from an aqueous solution. In another study, Koyuncu (2022) [30] converted *Capsicum annuum* L. into activated carbon for the removal of methanol yellow and methylene blue. On the other hand, Wang et al. (2023) [31] used activated carbon from chilli straw prepared by sequential carbonisation and K_2CO_3 activation for the adsorption of cationic methylene blue and anionic methyl orange dyes.

Although few studies have been reported on the use of chilli peppers as a biosorbent for the removal of toxic metals, dyes and drugs from aqueous solutions. No study has been conducted on binary sorption of Cd(II) and Ni(II) using chilli pepper from aqueous solution. Since the chemical pretreatments can potentially alter the cell surface by either removing or masking the groups or exposing more metal ion binding sites, we investigated here the effect of acids (HCl and HNO_3) on the removal of Cd(II) and Ni(II) using chilli peppers as adsorbents and the comparison between the adsorption capacity of the raw and acid-treated chillies. To this end, various factors affecting sorption such as solution pH, initial metal ion concentration and time were investigated using the batch equilibration technique. Desorption studies on the recovery of Cd (II) and Ni(II) from the adsorbents are also discussed. The sorption capacity was compared with the other materials to classify the proposed chilli pepper as a potential adsorbent. However, despite the progress made in investigating and understanding the adsorption of toxic metals, this field is still advancing, and several aspects need to be continuously monitored, investigated and improved. Key factors such as cost and compatibility with industrial conditions need to be completely investigated to ensure the practical applicability of the material because this study was conducted on a laboratory scale. Further research is needed to fill these gaps and advance the development of efficient and cost-effective adsorbents for the removal of toxic metals.

2. Reagents and methods

2.1. Reagents

We bought the chilli pepper from the Vaderbijlpark market in Johannesburg, South Africa. Without purification, the following materials were used: sodium hydroxide (NaOH) ≥ 98.0 %; hydrochloric acid (HCl)≥ 37.0 %; nitric acid (HNO_3)−70 %, and cadmium nitrate [Cd $(NO_3)_2$] ≥ 99.9 %. Analytical grade chemicals were purchased from Merck South Africa.

2.2. Methods

2.2.1. Raw chilli pepper (R-CP) preparation

A 15 g bag of chilli pepper was cleaned and dried at 40 °C in the oven. After being ground into a powder in a blender, the dried pepper was designated as raw chilli pepper (R-CP).

2.2.2. Acid treated chilli pepper (AT-CP) preparation

After combining 12 g of RCP with 150 mL of HNO_3 and HCl, the mixture was mixed for 2 h. Distilled water was used to rinse the acidic mixture multiple times. After that, the slurry was dried for 24 h at 50 °C in an oven. Using various parameters (pH, concentration, temperature, point of zero charge, and time), dried chilli pepper was employed as an adsorptive material for the adsorption of Ni(II) and Cd(II) ions. The acid-treated chilli pepper (AT-CP) was the sample's name. The preparation scheme is displayed in Fig. 1.

2.2.3. Batch adsorption studies

Metal solutions were prepared using nickel nitrate [$Ni(NO_3)_2$] and cadmium acetate salt $Cd(CH_3COO)_2$. Using a standard solution of 100 mg/L, the effect of contact time and other parameters were investigated and can be viewed in Table 1. A volume of 20 mL of the standard solution was poured into sample holders with 0.1 g of each material. Using 20 mL of working solution, the concentration effect was investigated for 60 min at various concentrations (Table 1). The adsorbent (0.1 g) was added in at various concentrations. With 20 mL of the working solution, which had 0.1 g of the material, the effect of pH was tested at various pH values as indicated in Table 1. Temperature effect was investigated using weighed (0.1 g) of each adsorbent into sample holders and 20 mL of standard solution at various temperatures, as indicated in Table 1 were investigated. For each parameter (pH, concentration, temperature, and time), an orbital shaker was utilized to equilibrate the adsorbent and working standard at 200 rpm. Glass wool was used to filter the solutions following each experiment. The solutions were removed in order to analyse the remaining Ni(II) and Cd(II) ions. Using ICP, the concentrations of the solutions were determined for both adsorbents (R-CP and AT-CP).

The Eq. (1) shown is used to assess the adsorption capacity, q_e in (mg/g) of Ni(II) and Cd(II) ions.

$$q_e = \frac{(C_o \;--\; C_e)\;V}{W} \tag{1}$$

(q_e) is the adsorption capacity, initial and final concentrations are represented by C_o and C_e (in mg/L) respectively. Solution volume and adsorbent mass are indicated by v (in mL) and W (in g) respectively.

2.2.4. Reusability studies

50 mL sample holders were filled with 0.1 g of the adsorbents. After adding 20 mL of the Cd/Ni solution to each container, they were left to agitate for two hours. The mixture was centrifuged for 15 min. This was considered the initial step, and ICP was used to analyse the outcomes. In the same sample holder 20 mL of a 0.04 M HCl solution was added and shaken for one hour and centrifuged for 15 min. Next, the HCl solution was taken out. After that, 20 mL of the Cd/Ni solution was added, shaken for two hours, and centrifuged for fifteen minutes. This action was done as the first cycle. Six times, these actions were carried out.

3. Characterization methods

The 4000 Nicolet FTIR spectrometer was used to determine the functional groups. A Tescan Mira scanning electron microscope was used to capture morphologies of AT-CP and R-CP. Using nitrogen at temperatures between 30 and 900 °C, Perkin Elmer's TGA 4000 was used to determine thermal analyses. The remaining Ni(II) and Cd(II) ions concentration was examined using an iCAP 7000 plus series ICP-OES spectrometer. The leaching test was carried out using a UV–Vis spectrophotometer (Lambda 25 from Perkin-Elmer), which records spectra in the UV and visible range from 180 to 1100 nm.

Table 1
Parameters used for adsorption for R-CP and AT-CP adsorbents.

Parameters	Ranges
Time effect	1,5,10,15,20,30,40,60,80 min
Temperature effect	30,40,50,60,70 °C
Concentration effect	20,40,60,80,100 mg/L
pH effect	1,3,5,7,9

4. Results and discussion

4.1. Characterization of AT-CP and R-CP

4.1.1. FTIR spectroscope

A flexible analytical method for identifying both organic and some inorganic materials is FTIR spectra. One of FTIR's advantages is its ease of use; small samples can be examined, and the spectra can be recorded in less than a minute, all thanks to the method's simplicity and minimal equipment adjustment requirements [32]. Fig. 2 shows the spectra, which were measured in the 4000–500 cm^{-1} region. For AT-CP and R-CP, respectively, the band peaks at 3275 and 3330 cm^{-1} show the presence of the –OH group stretching vibrations. Bands for the R-CP adsorbent's CH_3 and CH_2 groups, respectively, are located between

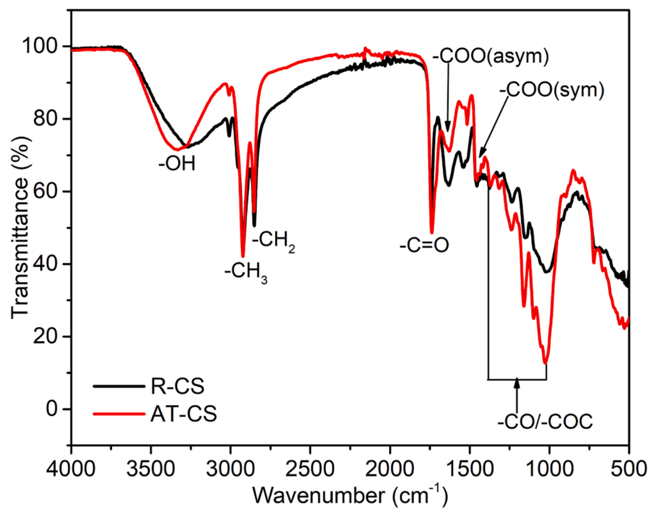

Fig. 2. FT-IR spectra of R-CP and AT-CP adsorbents.

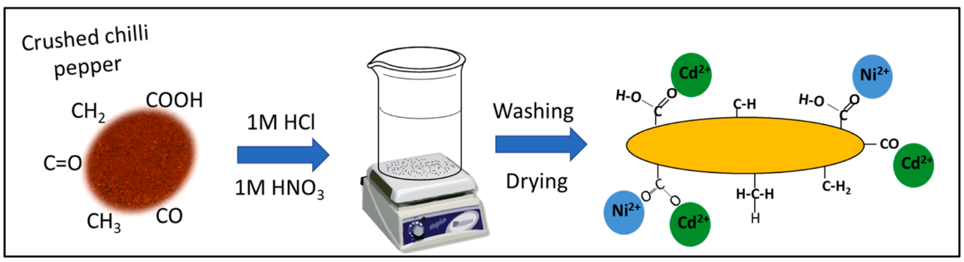

Fig. 1. Proposed preparation of AT-CP adsorbent.

2924 and 2852 cm^{-1} region. For AT-CP, these bands moved to 2917 cm^{-1} and 2861 cm^{-1}, respectively. On the R-CP adsorbent, the peak for C = O was 1744 cm^{-1}; on the AT-CP, it shifted to 1737 cm^{-1}. At 1636 and 1621 cm^{-1}, respectively, for R-CP and AT-CP, the asymmetric vibration of –COO was detected [33]. In contrast, the symmetric vibrations were detected at 1455 cm^{-1} for R-CP and 1454 cm^{-1} for AT-CP. The peaks at 1361 and 1336 cm^{-1} represent –COO and are attributed to symmetric stretching for R-CP and AT-CP, respectively [33]. The bands between 1300 and 1000 cm^{-1} region represent –CO and –COC [33]. Most bands revealed large oxygen-containing groups on the surfaces of AT-CP and R-CP. Peak shifting suggested a robust electrostatic interaction between the metal ions and the adsorbents [34,35].

4.1.2. SEM images

SEM was used for the determination of morphology for AT-CP and R-CP and can be observed in Fig. 2. Images in Fig. 3(a-b) for R-CP demonstrate that the surfaces are made up of particles that resemble spheres. The AT-CP images in Figures (d) and (e) show a variety of shapes, some of which are square-like and others of which have triangle and squares-like shapes that combine to form a structure that resembles a net. The treatment with acid, which is expected to enhance the uptake of Ni(II) and Cd(II) ions, may have caused the morphological change. The adsorbents are primarily composed of C and O components, according to the EDX results in Fig. 3(c) and (f), and Figure (c) of R-CP shows traces of K, P, Na, Mg, S, and Si, all of which are found naturally in plants. On the AT-CP, only C and O are visible following the acid treatment, as shown in Figure (f). The removal of the majority of these elements may have resulted from an ion-exchange process involving these elements and Ni(II) and Cd(II) ions [36].

4.1.3. Thermo gravimetry determination

Fig. 4 shows the TGA profile of R-CP and AT-CP adsorbents. The TGA profile revealed an increase in the thermal degradation of the AT-CP and R-CP components between 34 and 140 °C, which may be related to the adsorbents' water loss. The lignin, cellulose, and hemicellulose materials, which transpired between 140 and 478 °C, are responsible for the subsequent stage of degradation. It has been determined that these three compounds account for most of the mass loss during the heating process [37]. The residual mass loss in this second stage of decomposition is roughly 67.42 %. The AT-CP and R-CP's main component was cellulosic material, as shown by the thermal analysis. The findings of this study align well with the findings of Changmai et al. (2018) [38].

4.2. Physicochemical characterization AT-CP and R-CP

4.2.1. pH effect

In the adsorption process, the pH value of the solution is important in order to achieve a high adsorption capacity (qe) [39]. The pH effect for AT-CP and R-CP was investigated in a pH range from 1 to 9. The change in pH was measured while the other parameters were kept constant. The solutions and the adsorbents were equilibrated for 60 min. Fig. 5(a) shows that the sorption capacity for Cd(II) ions increases from pH 1 to 5. The same observation was made for Ni(II) ions, as shown in Fig. 5(b). The result illustrates that the adsorption of AT-CP and R-CP for Ni(II) and Cd(II) ions is strongly impaired in acidic medium. With increasing pH, the adsorption of AT-CP and R-CP increased, and the maximum adsorption performance was reached at pH 7.0. At neutral pH, the adsorption of AT-CP and R-CP decreased sharply due to hydroxyl group competition, as shown in Fig. 5(a-b) [40,41]. Based on the high uptake at pH 7.0, this suggests that the removal of Ni(II) and Cd(II) ions could be used as the optimum pH when using chilli pepper adsorbents. Similar results were obtained in the study of Awual (2016) [42] during the capturing of Pb(II).

4.2.2. pH at point zero charge effect

The performance of AT-CP and R-CP and the nature of the active sites of their surfaces can be characterised by the point of zero charge (pH_{PZC})- [43,44]. According to Fig. 6, the pH at the point of zero charge for AT-CP and R-CP is 8.29. To explain the electrokinetic properties of the AT-CP and R-CP surface, the point of zero charge is generally used [45] When the pH of the solution is lower than the pH_{PZC}, the presence of positive charges on the AT-CP and R-CP surface is expected. At pH_{PZC}, AT-CP and R-CP have the same amount of positive and negative charges, which prevents the adsorption of ionic species [46-48].

4.3. Adsorption results of AT-CP and R-CP

4.3.1. Temperature effect and thermodynamics

The effect of temperature on the sorption of Cd(II) and Ni(II) was carried out at five different temperatures, namely 30, 40, 50, 60 and 70 °C for R-CP and AT-CP. Fig. 7(a-b) shows that the removal of Cd(II) and Ni(II) ions increased with the increase of temperature. The increase in temperature indicates that the adsorption of Cd(II) and Ni(II) by R-CP and AT-CP favours high temperature. Similar trends were observed in the study by Liu et al. (2024) [49]. An increase in temperature indicates endothermic adsorption of both Cd(II) and Ni(II) [50].

Table 2 shows the thermodynamic parameters (ΔH^o, ΔS^o and ΔG^o) for Cd(II) and Ni(II) ions. The data were generated at temperatures of 303, 313, 323, 333 and 343 K. The (ΔG^o) values for Cd(II) and Ni(II) are negative at all temperatures and become less negative with increasing temperature, indicating that the sorption process is spontaneous and that the degree of spontaneity decreases with increasing temperature due to physisorption rather than chemisorption [50,51]. Ni(II) and Cd (II) ions uptake processes exhibit positive values for (ΔH^o), indicating endothermic reactions [52,53]. When the temperature of the system increases, an endothermic reaction increases the sorption of metal ions; this is consistent with the studies on the temperature effect conducted by Mabungela et al. (2022) [54]. The positive value of (ΔS^o) could be due to the escape of solvated H_2O from the metal ions into the solution during adsorption [49].

4.3.2. Contact time effect and kinetics

The effect of the reaction time between the adsorbents and the pollutants from the aqueous solution was evaluated to determine the equilibrium adsorption. A series of batch contact time experiments were performed to determine and evaluate the equilibrium adsorption capacity of Cd(II) and Ni(II) ions and the solution was analysed after each time interval after stirring. Fig. 8(a-b) shows the removal rate trends for Cd(II) and Ni(II) ions on R-CP and AT-CP absorbents. The data show that the adsorption of Cd(II) and Ni(II) ions is rapid in the first few minutes of contact time. With increasing contact time, the adsorption capacity increased and the adsorption equilibrium was reached after 40 min. Therefore, a contact time of 60 min is sufficient for this study to reach equilibrium. It can be assumed that the adsorption of Cd(II) and Ni(II) ions on R-CP and AT-CP absorbents occurs mainly by intraparticle diffusion and adsorption reaction mechanisms. Similar observations were made by Awual et al. 2020 [55] using a composite material to remove Ni(II) in aqueous solution.

The sorption rates of metals in aqueous solution can be evaluated using kinetic models. The mechanisms of the sorption process were determined by applying nonlinear kinetic models, in particular PFO and PSO, to the adsorption rates determined for Cd(II) and Ni(II) ions on R-CP and AT-CP adsorbents. The kinetic parameters of PFO and PSO are listed in Table 3. The PFO or PSO model, together with the correlation between the value, which is closer to (1), and the (qe) values, describes the evaluation of the sorption process. When comparing the PFO and PSO correlation values of the adsorbents, it was found that all adsorption processes gave better PFO values, with correlation values closer to (1). The PFO model assumes that the rate-limiting step of the adsorption process is related to the adsorption capacity of the adsorbent used. The PSO kinetic model assumes that the rate-limiting step of adsorption is chemical adsorption [56]. Thus, the attraction of van der Waal forces is

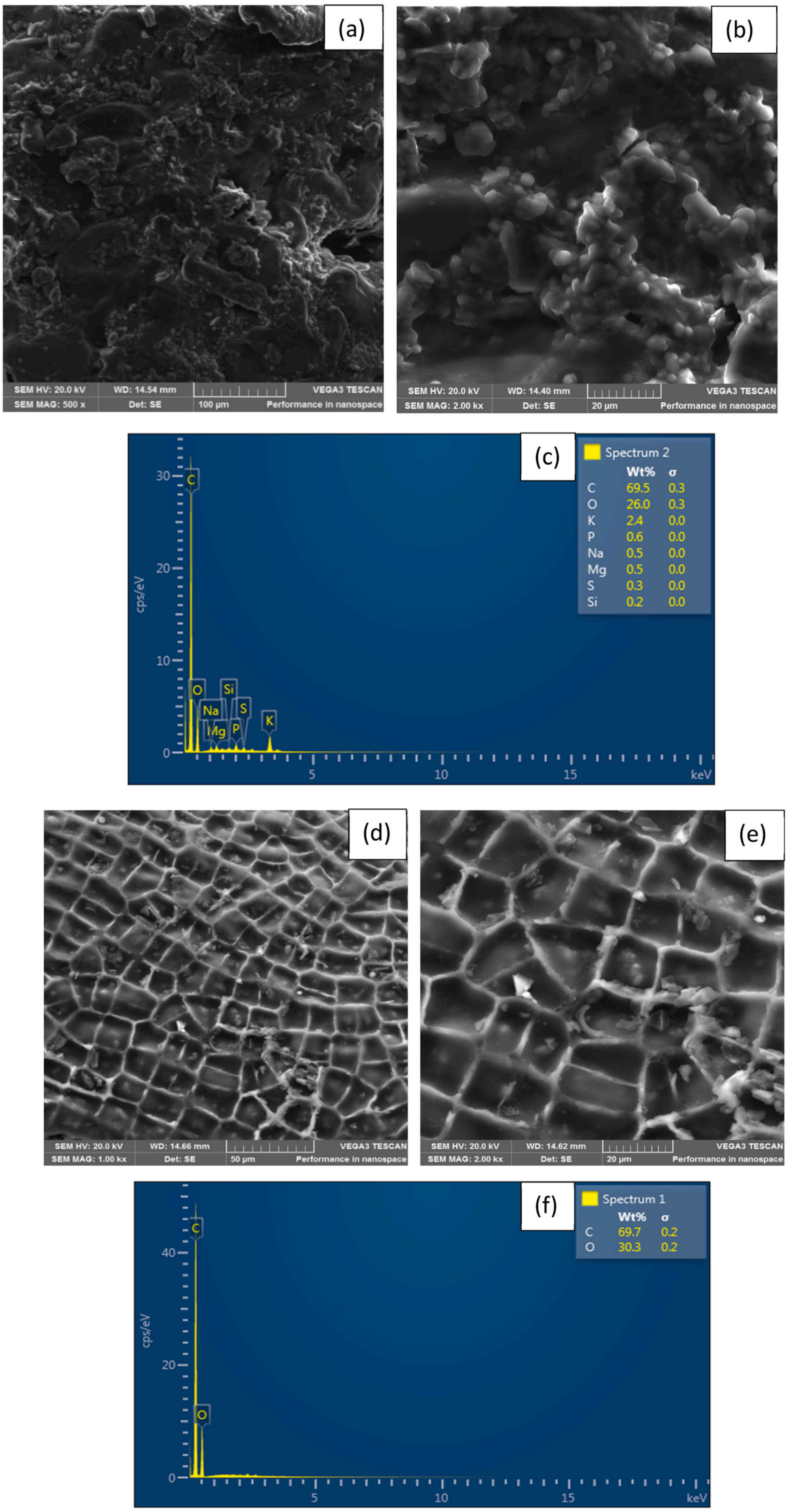

Fig. 3. SEM images and EDX spectra of (a-c) R-CP and (d-f) AT-CP adsorbent.

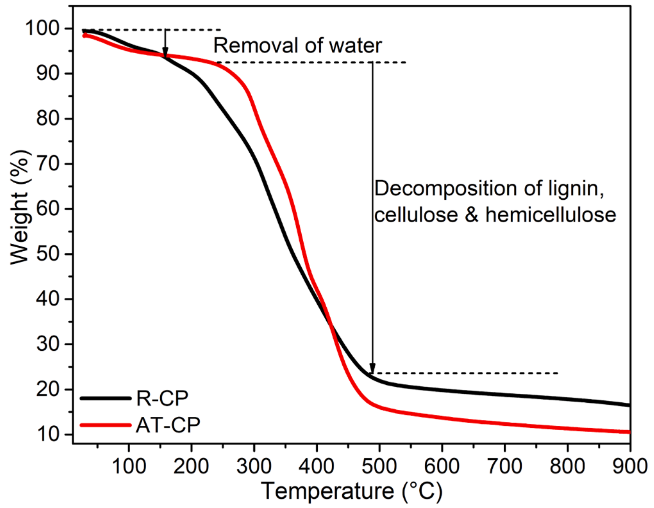

Fig. 4. TGA profile of R-CP and AT-CP adsorbent.

the basis for the sorption of Cd(II) and Ni(II) ions onto AT-CP and R-CP absorbents, as shown by a good fit of the PFO model [55,56]. This also indicates that the adsorption process of Cd(II) and Ni(II) ions on R-CP and AT-CP is an endothermic reaction [57].

4.3.3. Concentration effect and adsorption isotherms

The adsorption performance of AT-CP and R-CP for the removal of Cd (II) and Ni(II) ions was evaluated based on the adsorption amount and the removal amount at different initial concentrations. The uptake of Cd (II) and Ni(II) ions at different cation concentrations is shown in Fig. 9(a-b). The general trend of the graphs shows that the capacity increases with increasing concentration of Cd(II) and Ni(II) ion solution. As the initial concentration of Cd(II) and Ni(II) ions increased, the amount of adsorption by R-CP and AT-CP increased due to the driving force to overcome the mass transfer resistance between the liquid phases and the solid phase [58,59]. Chilli pepper therefore offered greater potential for the adsorption efficiency of Cd(II) and Ni(II) ions. However, as the concentration increased, the active sites on the adsorbents became saturated and equilibrium was reached.

Table 4 illustrates how the concentration effect results were subjected to nonlinear isotherms, namely the Langmuir and Freundlich models, to better understand the interaction of Cd(II) and Ni(II) ions with R-CP and AT-CP. The results in Table 4 show that the Freundlich isotherms are a better fit for both the Cd(II) and Ni(II) ions on AT-CP and R-CP. The R^2 values for the Langmuir model were lowest for both adsorbents. The application of the Freundlich isotherm model suggests that the multilayer deposition on the AT-CP and R-CP surfaces is the cause of the adsorption process [60,61]. Cd(II) and Ni(II) ions exhibit the highest value of K_f as shown in Table 4. It is possible that Cd(II) and Ni(II) ions are more easily coordinated with the active sites of the adsorbents [61]. The adsorbents produced showed higher capacity values under these experimental conditions and are therefore favorable from an ecological and practical point of view. Compared to some other adsorbents reported in the literature as indicated in Table 6, AT-CP and R-CP can achieve a relatively high sorption capacity.

5. Post adsorption process

5.1. Regeneration and reusability

The process of recovering the sorption capacity of used adsorbents for several cycles is known as regeneration of exhausted sorbent [62]. Fig. 10 illustrates the analysis of the reusability of AT-CP and R-CP adsorbents over six cycles of adsorption-desorption. Adsorbents loaded with Cd(II) and Ni(II) ions were effectively regenerated using 0.1 M HCl solution. The regenerate R-CP and AT-CP did not significantly lose

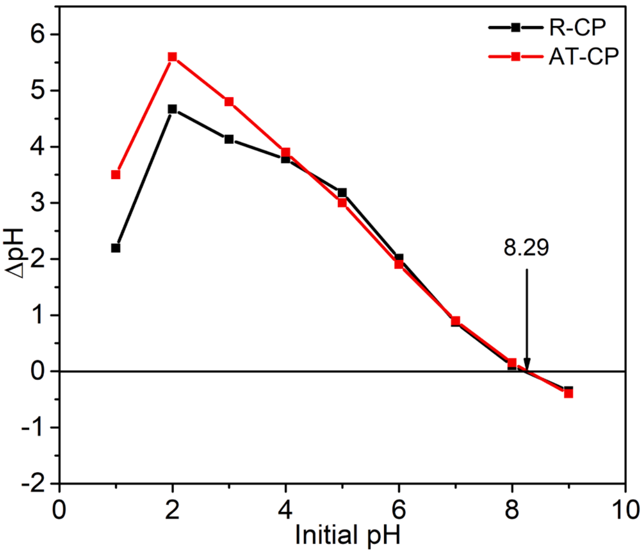

Fig. 6. Point zero charge of AT-CP and R-CP.

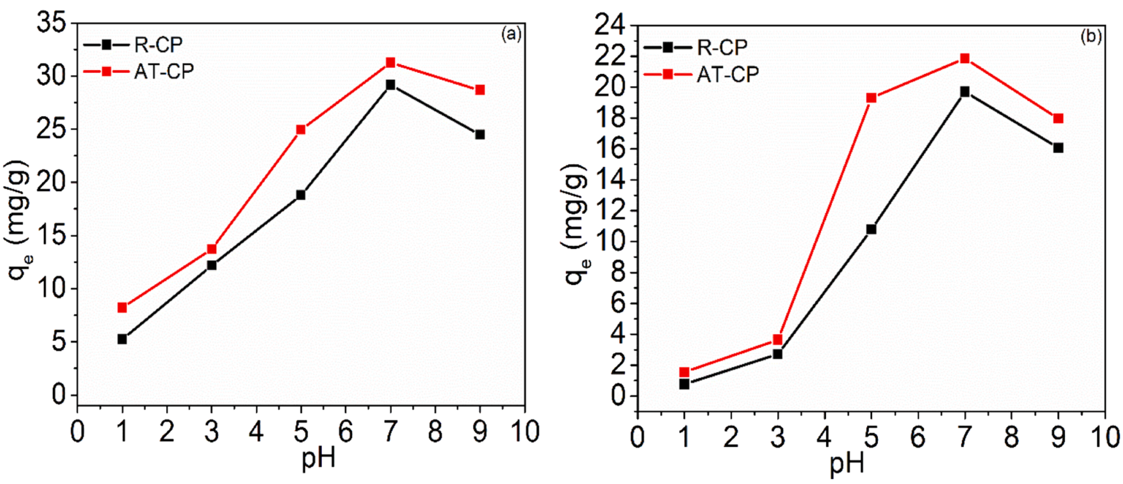

Fig. 5. pH effect (a) Cd(II) and (b) Ni(II) ions.

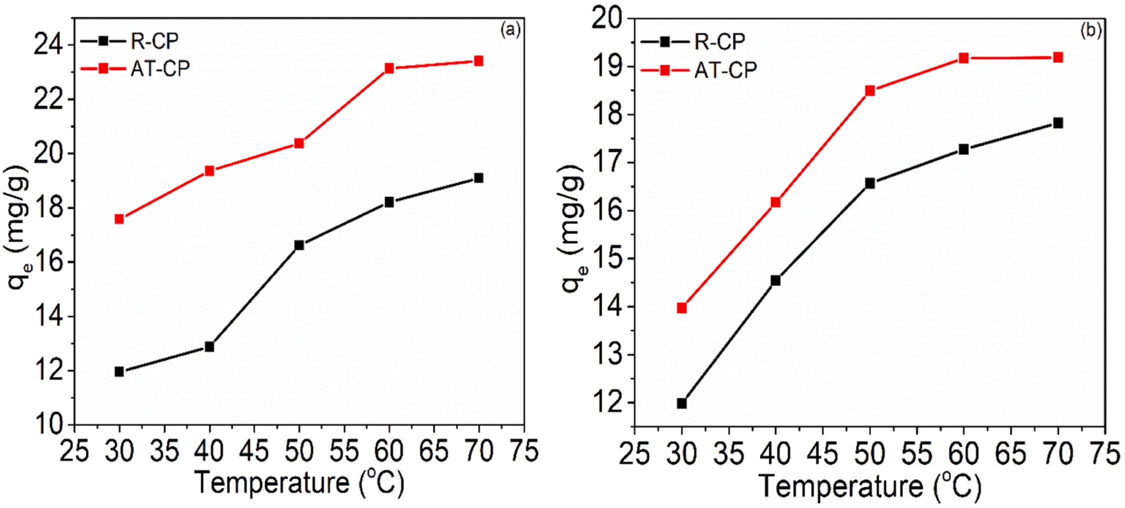

Fig. 7. Temperature effect on (a) Cd(II) and (b) Ni(II) ions.

Table 2
Thermodynamic studies and their parameters.

Parameter	AT-CP		R-CP	
	Cd(II)	Ni(II)	Cd(II)	Ni(II)
ΔH^o (KJ/mol)	8×10^{-3}	7×10^{-3}	4×10^{-4}	8×10^{-4}
ΔS^o (KJ.mol/K)	$2.\ 2 \times 10^{-3}$	2.3×10^{-3}	2.7×10^{-3}	2.2×10^{-3}
ΔG^o (KJ/mol) 303 K	−35.73	−36.24	−38.92	−38.41
313 K	−34.46	−35.43	−36.12	−33.96
323 K	−33.50	−31.41	−29.06	−31.51
333 K	−28.26	−28.96	−23.23	−14.53
343 K	−27.88	−21.59	−14.23	−13.21

capacity when they were used again for different cycles. For the adsorbents R-CP and AT-CP, there was no significant drop in sorption capacity. Following the fifth cycle, AT-CP's efficiency for Cd(II), Ni(II) ions, and R-CP was roughly 50 % lower. These findings lead to the conclusion that chilli peppers are economically sustainable due to their high regeneration and reusability rates.

5.2. FTIR analyses

The FTIR spectra of AT-CP and R-CP after the adsorption of Cd(II) and Ni(II) ions were compared with one another in order to gain a better understanding of the interaction between chilli pepper adsorbents and pollutants. The results are displayed in Fig. 11. The graphs demonstrate the presence of oxygen-rich functional groups in the adsorbents, such as –OH, –C = O, –COO, –CO, and –COC, and Table 5 lists the changes along with corresponding wavenumbers. Following Cd(II) ions after adsorption on AT-CP, some functional groups have shifted to lower wavenumbers and others to higher wavenumbers except for the –CH for the $–CH_3$ that did not change. Similarly Ni(II) ions after adsorption on AT-CP, most peaks shifted to higher wavenumbers. Similar to this, on R-CP, peak shifting to lower and higher wavenumbers was seen following Cd(II) ions adsorption. Following Ni(II) ions sorption, the asymmetric

Table 3
Kinetics and their parameters.

Kinetic model		AT-CP		R-CP	
		Cd(II)	Ni(II)	Cd(II)	Ni(II)
PFO	q_e (mg/g)	19.94	14.25	17.37	11.16
	K_1 (min^{-1})	0.28	0.12	0.56	0.06
	r^2	0.9995	0.9982	0.9923	0.9986
PSO	q_e (mg/g)	45.45	19.31	42.08	17.20
	K_2 (g.mg/min)	1.0080	1.0010	1.009	0.0143
	r^2	0.8789	0.8656	0.8423	0.8598
Experimental $q_{e,}$ (mg/g)		21.84	14.99	18.86	11.19

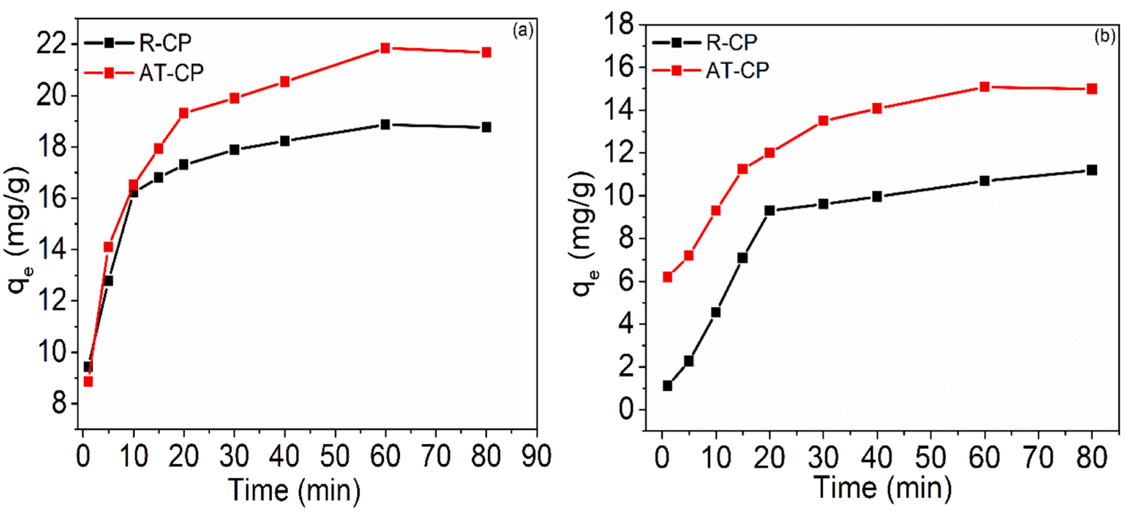

Fig. 8. Contact time effect (a) Cd(II) and (b) Ni(II) ions.

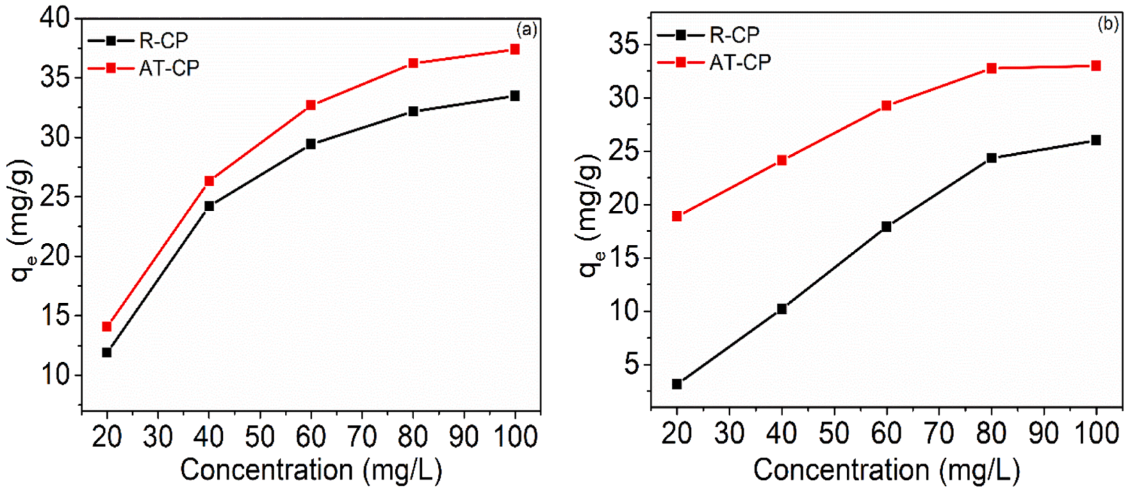

Fig. 9. Concentration effect (a) Cd(II) and (b) Ni(II) ions.

Table 4
Isotherms studies and their parameters.

Isotherm model		AT-CP		R-CP	
		Cd(II)	Ni(II)	Cd(II)	Ni(II)
Langmuir	Q_o (mg/g)	29.33	18.16	26.23	27.61
	b (L/mg)	0.0223	0.0329	0.0246	0.017
	r^2	0.8834	0.9717	0.8866	0.8990
Freundlich	q_e (mg/g)	38.33	50.30	38.10	39.12
	1/n	1.90	3.50	1.88	6.50
	k_f	2.831	2.62	3.10	2.771
	r^2	0.9903	0.9980	0.9959	0.9967
Experimental q_e, (mg/g)		37.36	19.20	37.38	32.99

and the symmetric peaks shifted to higher wavenumbers. Peaks that shift and suggest that these functional groups were involved in the uptake of Ni(II) and Cd(II) [63,64].

5.3. Adsorption mechanism

Adsorption of pollutants from wastewater is a process that involves the diffusion of pollutant molecules and their electrostatic attraction on the surface of the adsorbent [65]. Understanding the adsorption mechanisms of chilli pepper-based adsorbents is important for current and future studies. The available literature on the adsorption of various toxic metal ions with adsorbents suggests that the uptake mechanisms are determined by various processes such as diffusion, electrostatic interactions, hydrogen bonding, diffusion within particles, redox interactions, complexation, ion exchange, precipitation, and pore adsorption [66]. In this study, the FTIR data were analysed before and after adsorption to understand the removal of Cd(II) and Ni(II) ions by the adsorbents. FTIR confirmed the presence of groups such as hydroxyl (-OH), carbonyl (-C = O) and carboxyl (-COO) on AT-CP and R-CP adsorbents. During the adsorption of Cd(II) and Ni(II) ions, electrostatic interaction took place between the interaction of Cd(II) and Ni(II) ions with oxygen (O) from carboxyl (-COO) and carbonyl (-C = O) groups; also between (O) from the with hydroxyl (-OH) groups. In this work the possible proposed mechanism is electrostatic attractions between positively charged metal ions and negatively charged functional groups of AT-CP and R-CP adsorbents. Additionally, attractive forces such as hydrophobic interactions and van der Waal forces could be involved in the process of metal ions adsorption [67].

6. Stability of chilli pepper

The stability of chilli-based adsorbents in water treatment was investigated. The test was carried out by shaking R-CP and AT-CP in distilled water for 60 min. The solution was then analysed by UV–Vis spectrophotometer for traces of organic components that may have leached out. Fig. 12 shows that the distilled water and the water after

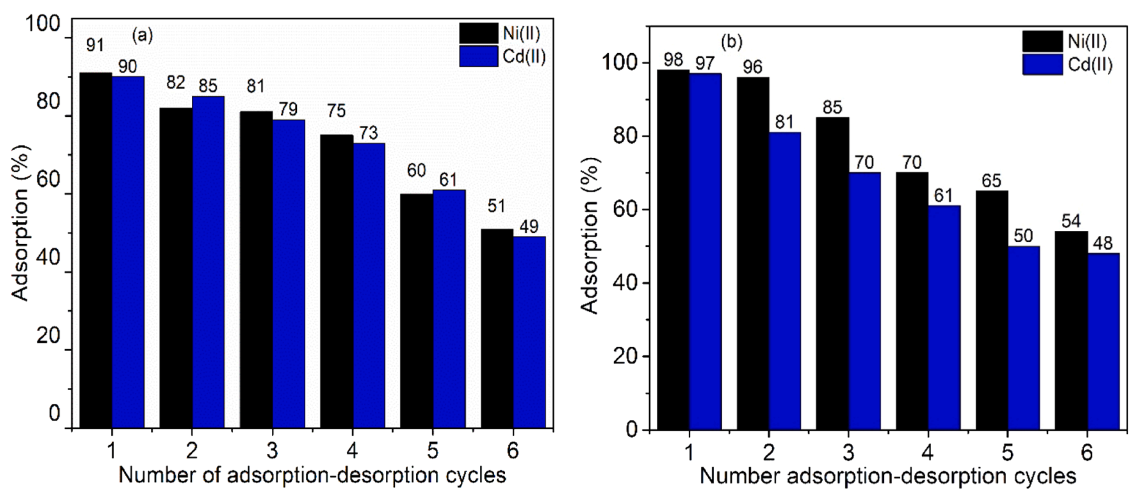

Fig. 10. Reusability of (a) AT-CP and (b) R-CP for six adsorption-desorption cycles.

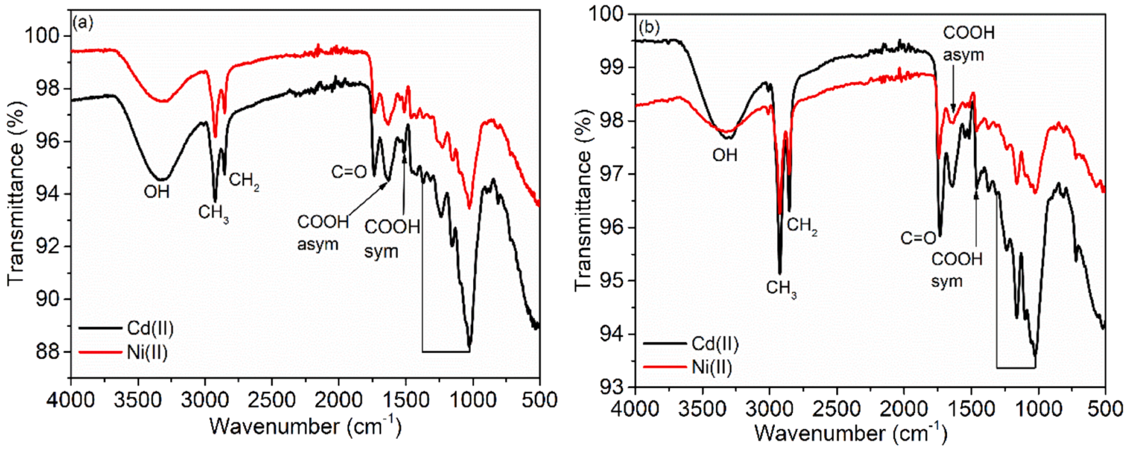

Fig. 11. FTIR spectra of (a) AT-CP and (b) R-CP adsorbents after the adsorption of Cd(II) and Ni(II) ions.

Table 5
FTIR data of AT-CP and R-CP before and after adsorption.

Functional Groups	AT-CP			R-CP		
	Before adsorption	After adsorption		Before adsorption	After adsorption	
		Cd (II)	Ni (II)		Cd (II)	Ni (II)
–OH	3330	3328	3340	3275	3298	3322
–CH of CH_3	2917	2922	2923	2924	2924	2928
–CH of CH_2	2861	2846	2852	2852	2845	2857
–C = O	1737	1734	1746	1744	1728	1751
–COO (Asym)	1621	1629	1634	1636	1628	1640
–COO (Sym)	1454	1511	1504	1455	1457	1563

Table 6
Comparison study of adsorption capacity of Cd(II) and Ni(II) ions for different sorbents.

Adsorbent	qe (mg/g)	Pollutant	References
Activated carbon-Pomegranate husk	68.60	Cd(II)	[68]
Modified pomegranate husk	46.29		[69]
Chilli pepper	37.36		**This study**
Carbon nanotubes-Fe_3O_4	23.80		[70]
Rice husk biochar	17.80		[71]
Aphanothece sp. dried biomass	12.24		[72]
Waste of myrica	5.61		[73]
Oak wood carbon-Fe_3O_4	2.90		[74]
Raw sludge	163.6	Ni(II)	[75]
Vermiculite	47.85		[76]
Chilli pepper	33.34		**This study**
Cashew nut shell	18.86		[77]
Lemon peel	15.36		[78]
Cement brick waste	5.60		[79]
Silty clay	3.60		[80]
Green tea waste	0.31		[81]

rinsing the samples are similar and no new peaks observed. This indicates that the samples are stable and can be safely used as absorbents.

7. Comparison studies

Table 6 shows the uptake capacities for Cd(II) and Ni(II) on AT-CP adsorbent that were obtained and compared with other reported materials. In comparison to certain materials, AT-CP's results indicated a higher sorption capacity. According to the data, different pollutants can be adsorbed by AT-CP adsorbent in water treatment applications. This study indicate that chilli pepper has a potential for commercial use.

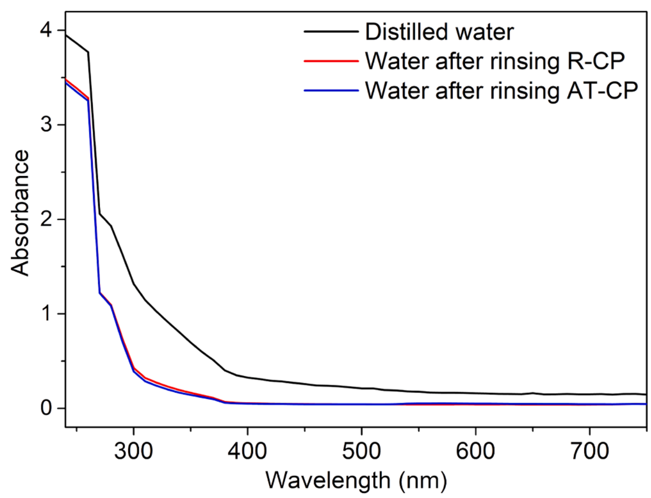

Fig. 12. UV–Vis spectra of AT-CP and R-CP adsorbents.

8. Conclusions

In this study, acid-treated chilli pepper material was prepared for the removal of toxic Ni(II) and Cd(II) ions for environmental remediation. The prepared adsorbent is the first one prepared from the combination of nitric acid and hydrochloric acid for binary adsorption of Ni(II) and Cd(II) ions. The adsorption capacity of the acid-treated chilli pepper adsorbent was compared with raw chilli pepper adsorbent. The results showed that the pH, concentration, time, and temperature of the metal ion solutions were parameter dependent for both adsorbents. The peaks from FTIR spectroscopy showed that the adsorbents had functional groups containing oxygen. SEM images of AT-CP showed a combination of different shapes forming a net-like structure, while the surface of R-CP consisted of spheres. The adsorption of Ni(II) and Cd(II) ions was influenced by pH. The sorption capacities of both adsorbents increased with temperature and reached their maximum capacity at 70 °C. The effect of time showed that the maximum sorption capacity for both adsorbents was reached at different times. The concentration effect showed that as the concentration of Ni(II) and Cd(II) ions increased, the adsorption capacity for both adsorbents also increased. Based on the adsorption capacities, acid-modified chilli pepper was the best adsorbent compared to raw chilli pepper. Binary adsorption of Ni(II) and Cd (II) ions from aqueous solution using chilli peppers modified with a mixture of nitric acid and hydrochloric acid was found to be effective. Compared to other methods of acid modification, the present work has shown that the adsorbent prepared from two different acids have the advantage of removing toxic metal ions and achieving high sorption capacities. Therefore, the adsorption process is proposed as an efficient, fast, and simple technique for the uptake of pollutants from aqueous solutions. We therefore hypothesise that this adsorbent could serve as an effective material for the removal of Ni(II) and Cd(II) ions in the water environment.

CRediT authorship contribution statement

Conceptualization, Software, Methodology, Supervision, writing review and editing by **PM Thabede**. Formal analysis, Investigation, Writing original draft by **N. Nkosi**. Supervision, Validation, Resources, Project administration by **N.D Shooto**. Characterization, Data curation by **P. Nyamukamba**. All authors have read and agreed to the published version of the manuscript.

Declaration of competing interest

The authors declare that there is no conflict of interest.

Data availability

The findings for the work can be obtainable from authors upon request.

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