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Green Porous Composite for Combining Ion Exchange-Adsorptive Removal of Zinc Ions from Aqueous Solutions

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Abstract

A low-cost, effective green porous composite was prepared and used for the sorption of Zn^{+2} ions from aqueous solutions. The effect of contact time, sorbent dosage, initial ion concentration, solution pH, and temperature on the sorption of Zn^{+2} ions was investigated. The results showed higher removal efficiency of Zn^{+2} ions (83%), which was achieved at a contact time of 120 minutes, a normal pH of 6.4, and a temperature of 313 K. The Langmuir isotherm model successfully described the experimental results of the sorption process with a theoretical maximum sorption capacity of 4.819 mg/g. The kinetics of sorption showed that the pseudo-second-order model fitted the experimental results better than the pseudo-first-order model. The intra-particle diffusion kinetics indicated that the boundary film was the rate-determining step of the sorption process. The thermodynamic parameters showed that the sorption of Zn^{+2} ions was spontaneous and endothermic under the studied conditions. The solidification of spent composite by kaolin was able to keep the leachate cations at an acceptable level in the solution after 12 weeks of exposure to a salty medium.

Keywords: Adsorption, Isotherms, Green materials, Thermodynamics, Zinc ions, Kinetics.

خليط مسامي أخضر للإزالة المتلازمة لأيونات الزنك من المحاليل المائية بالتبادل الأيوني–الامتزاز

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الخلاصة

تم تحضير وأستخدام مركب مسامي أخضر منخفض التكلفة لأمتزاز أيونات الزنك من المحاليل المائية. تم دراسة تأثير زمن التلامس ، جرعة المادة المازة ، تركيز الأيونات الأبتدائي، الأس الهيدروجيني للمحلول ودرجة الحرارة على أمتزاز أيونات الزنك. أظهرت النتائج أن كفاءة إزالة (83٪) لأيونات الزنك قد تحققت في زمن تلامس قدره 120 دقيقة ، ودرجة حموضة طبيعية 6.4 ودرجة حرارة 313 كلفن. وصف أنموذج لانكماير بنجاح النتائج التجريبية لعملية الأمتزاز بقدرة أمتزاز نظرية قصوى تبلغ 4.819 مجم / جم. أظهرت حركيات الأمتزاز أن أنموذج الدرجة الثانية الزائف يناسب النتائج التجريبية بشكل أفضل من أنموذج الدرجة الأولى الزائف. أظهرت حركية الانتشار داخل الجسيمات أن الطبقة الحدودية كان الخطوة المحددة لسرعة عملية الأمتزاز. أظهرت المعلمات الدينمية الحرارية أن أمتزاز أيونات الزنك كان تلقائيًا وماصًا للحرارة في ظل

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الظروف المدروسة. وأنه بالأمكان تجميد المركب المستهلك بواسطة الكاولين من أجل أبقاء الراشح من أيونات المعدن الموجبة عند مستوى مقبول في المحلول بعد 12 أسبوعًا من تعريضه الى وسط مالح.

1. Introduction

Over the decades, increasing industrial activities and population growth have made access to usable water challenging [1]. Hence, increased demand for services and food production has increased waste release, pollution, and the deterioration of natural water sources, affecting safe drinking water availability [2,3]. Heavy metals, including Cu, Ag, Zn, Cd, Hg, Pb, Cr, Mo, Mn, Co, Ni, etc., are among the pollutants severely harming natural water supplies. Heavy metals are the most controversial pollutants because they are discharged with wastewater from many industrial operations [4,5]. Heavy metals are hazardous because they are responsible for some diseases such as lung cancer and malignancies of other respiratory organs, kidney and bladder cancer, brain and reproductive organ damage, and heart and immune system issues [6]. Vital to human health is treatment to eliminate or reduce heavy metals in potable water to acceptable levels [7]. Zinc levels in the waste range from less than 1 to more than 48,000 mg L^{-1}. Polluted discharges from agricultural activities, sediment remobilization or entrainment, groundwater intrusion, a combination of these sources cause substantial levels of zinc release into the environment [8]. Heavy metals can be removed from wastewater using different technologies, including evaporation, coagulation, foam flotation, chemical precipitation, solvent extraction, electro-deposition, cementation, sedimentation, ion exchange, adsorption, and membrane separation processes [9,10]. Adsorption and ion exchange are excellent methods for minimizing heavy metal contamination. Zeolites are excellent materials to be used in the removal of heavy metals by ion exchange due to their uniform microporosity, high specific surface area, high concentration of exchangeable cations, hydrothermal stability, and other surface properties [11,12]. Zeolites are microporous hydrated aluminosilicate minerals with exceptional ion exchange properties [13]. Zeolites are non-toxic and environmentally safe [14]. Their structure is built from a three-dimensional network of SiO_4^{+4} and AlO_4^{-5} tetrahedrons linked by shared oxygen atoms [15]. Sodium, potassium, or calcium cations balance the structure's negative charge, and they can be exchanged with other cations [16]. Zeolite’s usage on a broad scale has some limitations because its efficiency is affected by the weak diffusion of species inside its micropores [17]. Work is ongoing to reduce diffusion imperfections by creating hierarchically porous structures made of zeolites [18,19]. Hierarchically porous structures are materials containing two or more porosity levels, regardless of pore homogeneity at each level [20]. The hierarchically porous zeolites have a more extensive porous system than conventional zeolites, which improves access, molecules transport, and mass transfer problems [21]. This can be achieved by depositing a thin layer of zeolite crystals over a meso- or macroporous support, with the option of removing this support after the preparation step. Finding an appropriate approach to tailoring different porosity levels is critical to maximizing the benefits of the hierarchically porous structure and zeolite activity [22,23]. Many supports and templates have been used to synthesize such materials, but some of them are expensive and removed by post-synthetic calcination, which is wasteful and costly [24,25]. It is essential to find a low-cost porous material to act as a support for a particular hierarchically porous material. As a result, using waste biomass as a source of porous supports has emerged as trends toward reducing the amount of solid waste disposed of in the environment and producing effective, low-cost porous supports. In the context of this work, a green method of synthesis of hierarchically porous zeolite-carbon composite will adhere the nanosized zeolite having low Si/Al to porous support without the aid of further thermal treatment, which was previously used in the other methods, thus keeping the original zeolite crystallinity. This method is defined as green because it uses a polymeric admixture to anchor zeolite nanocrystals over the support surface with no thermal treatment and reduced energy consumption. In this study, a green hierarchically porous zeolite-carbon composite sorbent, which was previously synthesized using an eco-friendly method, will be used in the studies involving the removal of zinc ions from aqueous solutions at different conditions such as contact times, initial ion concentration, sorbent dosage, pH, and temperature of the ion's solution. Also, sorption kinetics, isotherm models, and thermodynamic parameters such as enthalpy change, entropy change, and Gibbs free energy change will be studied.

2. Material and methodology

2.1. Materials

The sorbents used in this work were NaX zeolite, plum stone shell carbon (PSC), and NaX zeolite-carbon composite (DFZPC), which were obtained from previous work [26]. The preparation of a green porous DFZPC composite was accomplished by allowing zeolite NaX nanocrystals to disperse in a mixture of *N*,*N*-dimethylformamide (M.wt. =73.09 g/mol) provided by Central Drug House (P) Ltd., Polyacrylonitrile (M.wt. =150000 g/mol) provided by Hangzhou Sartort Biopharma Co. Ltd., and Polyvinylpyrrolidone (M.wt. = 40000 g/mol). Then, this combination was mixed with PSC, washed, and filtered. More details about the synthesis method can be found in [26]. Zinc acetate ($(CH_3COO)_2Zn.2H_2O$, M.wt. = 219.50 g/mol), was provided by Central Drug House (P) Ltd. as a source of zinc ions. Sodium hydroxide (NaOH, 97% wt.) provided by HIMedia Laboratories Pvt. Ltd. and hydrochloric acid (HCl, 35-38% vol.) supplied by Central Drug House (P) Ltd. were used for changing solution pH. Sodium silicate (32-33% wt. SiO_2) was obtained from the Lab-UAE Company to prepare an activation solution. Sodium chloride (NaCl, 99.9% wt) was obtained from CDH. Kaolin powder as a geopolymer source was provided by TurboQuant-Powders. Distilled water was used to conduct this work.

2.2. Batch sorption experiments

Batch sorption was studied at different contact times, sorbent dosages, initial metal ion concentrations, solution pH, and solution temperature. The experimental study was performed in a 150 mL conical flask containing 100 mL of Zn^{+2} ion solution mixed with a certain weight of the adsorbent at a constant shaking speed of 200 rpm. The stock solution of zinc ions with a concentration of 500 mg/L was prepared by dissolving a specific weight of zinc acetate in distilled water (1 L). After that, the stock solution was used to prepare several solutions with concentrations ranging from 10 to 150 mg/L by dilution to study the effect of the initial concentration. The kinetic study was performed by changing the solution temperature (289-313 K) while keeping other parameters constant at an initial Zn^{+2} ion concentration of 50 mg/L, DFZCC dose of 1 g/100 mL, mixing speed of 200 rpm, solution pH of 6.2, and contact time of 120 minutes. After shaking for a specific time, samples were withdrawn using a sterile syringe filter (pore size 0.45 µm, diameter 25 mm) at different intervals, and the solid sorbent was removed from the liquid phase by filtration. The concentration of remaining ions was measured using an atomic absorption spectroscopy model Pg instrument, AA500. The final pH of the solution was measured in all the experiments using the MH-TECH pH meter. The removal percentage (%Removal) and sorption capacity (q_e) were calculated by Equations 1 and 2 [27–29]:

$$\%Removal = \frac{C_i - C_r}{C_i} \times 100\% \tag{1}$$

$$q_e = (C_i - C_e) \times \frac{V}{W} \tag{2}$$

where q_e (mg/g) is the mass of zinc ions removed per weight of a sorbent (W, g) at equilibrium, V is the volume of zinc ions solution (L), C_i, is the initial concentrations of zinc ions, and C_r and C_e are the remaining concentration of zinc ions in solutions (mg/L) at any time and at equilibrium time, respectively. Applying C_r in Eq. (2) instead of C_e will result in q_t which is the sorption capacity at different times. Table 1 shows the experimental conditions used in this work.

Table 1: The experimental conditions used for studying Zn^{+2} ion sorption

Study parameters	The experimental conditions
Contact time	Initial ion concentration = 50 mg/L, sorbent dose = 0.5 g/100 mL solution, mixing speed = 200 rpm, solution pH = 6.4, and room temperature = 289 K
Sorbent dose	Contact time = 120 minutes, initial ion concentration = 50 mg/L, mixing speed = 200 rpm, solution pH = 6.4, and room temperature = 289 K
Initial ion concentration	Contact time = 120 minutes, sorbent dose = 1 g/100 mL, mixing speed = 200 rpm, solution pH = 6.4, and room temperature = 289 K
Solution pH	Contact time = 120 min, initial ion concentration = 50 mg/L, sorbent dose = 1 g/100 ml, mixing speed = 200 rpm, and room temperature = 289 K
Solution temperature	Contact time = 120 minutes, initial ion concentration = 50 mg/L, sorbent dose = 1 g/100 ml, mixing speed = 200 rpm, and room temperature = 289 K

2.3. Solidification of waste sorbent

Examining the composite's ability to retain metal ions inside its porous structure to ensure secure discarding was performed by treating the waste sorbent with geopolymer. With some amendments, the geopolymer was made as described in published work [30,31]. The activator solution was made by blending NaOH solution (3 mL, normality 10 N) with sodium silicate solution (0.6 mL) for 15 minutes. Then, metal-bearing ion exchangers (0.3 g) and kaolin (3 g) were dry-mixed for 10 minutes to achieve a homogenous solid mixture. After that, the activator solution (2.5 mL) was added to the solid mixture and mixed for 15 minutes. The resulting slurry was then put into cast moulds. The curing process was carried out at room temperature overnight, followed by three days at 353 K. The metal leaching from the solidified samples was tested by immersing the solid samples (2 g) in NaCl solution (100 mL, 0.05 M). The concentration of ions leaching into the solution was detected by atomic absorption spectroscopy using the model Pg instrument AA500 after 1, 2, 3, 4, 8, and 12 weeks of contact time.

3. Results and discussion

3.1. Sorption experiments

3.1.1. Contact time

The effect of contact time on the percent removal of Zn^{+2} ions using sorption by DFZPC is shown in Figure 1a. The percent removal of Zn^{2+} ions initially had an upward trend to reach about 76.3%, but it stabilized at about 120 min. After that, an increase in contact time did not significantly change the removal percent, which indicates attaining equilibrium. The high percent removal at the initial time was due to the abundance of active sites on the sorbent's surface, which were used up with time and became saturated. Obtaining a moderated removal percent of Zn^{+2} ions from aqueous solution in this experiment can be attributed to Zn^{+2} ions' large hydrated radius because of their small ionic radius, affecting their charge density. The dipolar water molecules are assembled around the positively charged ions to form their hydrated shell. The cation with a larger hydrated radius poorly diffuses through the sorbent pores because it is difficult to strip the water molecules surrounding the cation. This means the cation has a lower charge density, which makes its removal from water more difficult. Figure 1a shows q_t increased in the same manner as removal percent. The adsorption performance of carbonous support PSC and pure NaX zeolite for Zn^{+2} ions was tested at the same conditions used for DFZPC. Surprisingly, PSC showed performance in the uptake of Zn^{+2} ions from water (Figure 1b). This performance of PSC can be attributed to the moderated preparation conditions and the preparation method for PSC mentioned in [26] that allowed activation of the PSC surface to produce an acceptable contact area for adsorption, contrary to that used in previous work [32]. Therefore, the total sorption capacity of DFZPC is attributed to the activity of NaX zeolite and PSC, i.e., the removal process combining both ion exchange rendered by NaX zeolite and adsorption rendered by PSC. Consequently, it can be said that DFZPC has dual functions. Furthermore, the pH of the solution slightly increased at the end of the removal process to 6.9, which can be attributed to the fact that DFZPC functions in the removal process were balanced at these conditions.

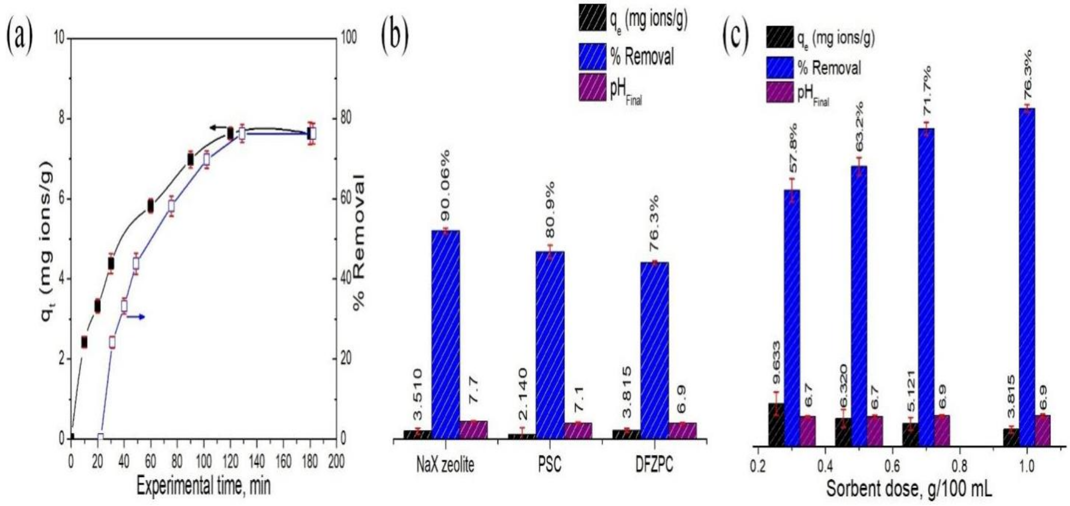

Figure 1: (a) Effect of contact time; (b) Study the sorpent type; (c) Effect of sorbent dosage

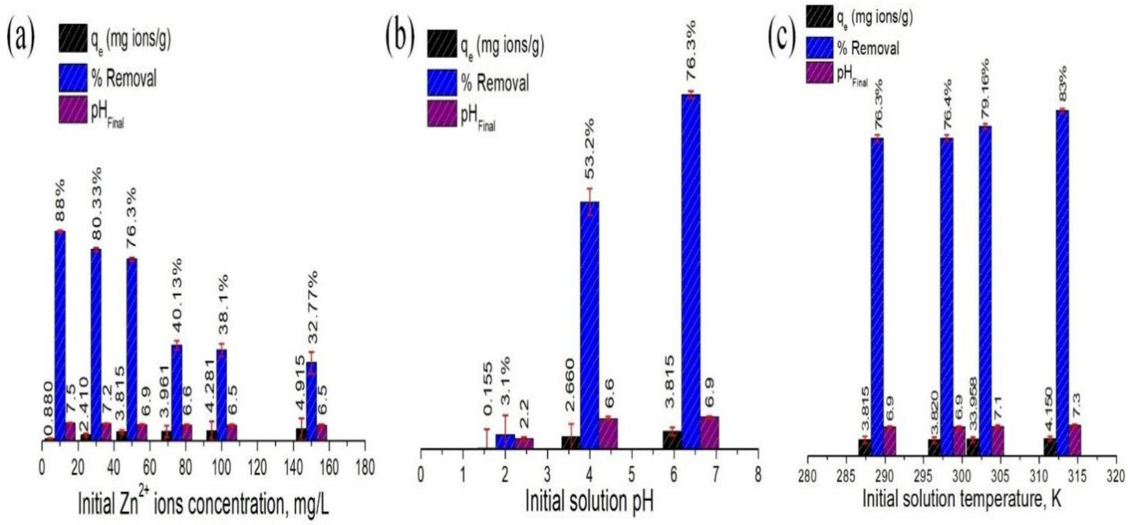

Figure 2: (a) Effect of initial ion concentration; (b) Effect of solution pH; (c) Effect of solution temperature

3.1.2. Sorbent dose

The results expressing the effect of DFZPC dosage on the percent removal of Zn^{+2} ions from water are shown in Figure 1c. The results showed that increasing the sorbent dosage from 0.3 to 1 g resulted in a higher percent removal of metal ions, from 57.8 to 76.3%. The increased percent removal with increasing DFZPC dose was because more DFZPC dose offered extra surface area and active sites to remove more cations. Also, the final pH slightly increased to 6.9, indicating equivalent roles for both ion exchange and adsorption in DFZPC at these conditions.

3.1.3. Initial ions concentration

The initial metal ion concentration is a critical factor in sorption studies because most contaminated wastewater contains varying quantities of metal ions. The results expressing the effect of initial metal ion concentration on the percent removal of Zn^{+2} ions by DFZPC are shown in Figure 2a. The percent removal of metal ions decreased from 80.33% to 32.77% as the initial metal concentration increased from 10 to 150 mg/L. This was due to the fact that the dose of DFZPC used for the same volume of the ion solution has a specified number of active sites and adsorption areas that are saturated with fairly equal ion concentrations even though they are used at high concentrations [33]. In other words, for a fixed DFZPC dose and a volume of the ion solution, increasing the concentration of ions means increasing the concentration of ions competing for the same number of active sites provided by the used sorbent dose, which causes a reduction in the removal efficiency because the sites become saturated by the ions. Also, Figure 2a shows a different trend of the pH at the end of the sorption process by changing the initial concentration.

3.1.4. Solution pH

The solution pH is one of the most influential variables controlling the sorption process, thus it must be investigated. The pH of the solution influences the surface charge of the sorbents as well as the degree of metal ionization and sorbate specification. The effect of pH on the percent removal of Zn^{+2} ions by DFZPC is shown in Figure 2b. The results show that the percent removal was low in an acidic medium but increased as the solution pH increased. When the pH was changed from 2 to 6.4, the percentage sorbed material increased from 3.1 to 76.3%. The percent removal was minimal at low pH values because the protons competed with metal cations for active sites in DFZPC. But the surface charge became approximately neutral at pH 6.0-6.9 to allow fair ion exchange of Zn^{+2} ions. According to the previous work [26], at a pH higher than the pH_{pzc} (6.9), the surface of DFZPC becomes negatively charged, which increases the adsorption of the positively charged metal ions through electrostatic forces of attraction [34]. However, it was not possible to raise the solution above 7 because the hydroxide of metal precipitates at this value. Figure 2b shows the final pH of the solutions, which increased from 2.2 to 6.9 with an increase in the initial pH of the solution from 2 to 6.4. This can be imputed to the predominance of the ion exchange process over the adsorption process, which favors electrostatic forces of attraction.

3.1.5. Solution temperature

The results explaining the effect of temperature on the percent removal of Zn^{+2} ions by DFZPC are shown in Figure 2c. The results show that the sorption of Zn^{+2} ions increased marginally when the temperature increased from 289 to 313 K. This suggests that a high temperature promotes the ion exchange activity of DFZPC and that the sorption is endothermic. This trend can be attributed to the reduction in the hydration shell surrounding the cations as temperature rises to allow the attraction between ions and the sorption sites. Figure 2c also shows that the final pH of the solution increased slightly from 6.4 to 7.3 due to the increase in temperature, which confirms that rising solution temperatures promote the ion exchange activity of DFZPC.

3.2. Sorption kinetics

Kinetic studies provide information about the uptake rates and rate-limiting steps such as external mass transfer, intraparticle mass transfer, and the adsorption process [35]. The most commonly used kinetic models are:

i- the pseudo-first-order kinetic model, which is written as given by Equation 3 [30]:

$$\ln(q_e - q_t) = \ln q_e - k_1 . t \tag{3}$$

Where k_1 is the pseudo-first-order rate constant (min^{-1}).

ii- the pseudo-second-order kinetic model, which is as given by Equation 4 [30]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}\, t \tag{4}$$

Where k_2 is the pseudo-second-order rate constant (g/mg.min).

iii- the Weber and Morris intra-particle diffusion model, which is given by Equation 5 [36]:

$$q_t = k_i . t^{0.5} + C_{ip} \tag{5}$$

Where k_i is the intraparticle diffusion rate constant (mg/g.min$^{0.5}$), and C_{ip} is a constant associated with the boundary layer thickness (mg/g).

Table **2** displays the computed rate constants and determination coefficients (R^2) of the models. It can be clearly observed that the fitting of sorption data of Zn^{+2} ions by the pseudo-second-order model with an R^2 value of 0.922-0.999 is better than that by the pseudo-first-order model. Also, the resulting values of sorption capacity from this model were very close to those obtained experimentally. This result indicates the sorption mechanism of Zn^{+2} ion removal by DFZPC includes a chemical reaction [37]. In addition, the results demonstrated successful fitting to the Weber and Morris intra-particle diffusion model with an R^2 of 0.976-1. Increasing the values of K_i with increasing temperature indicates enhancing the diffusion rate inside the DFZPC pore system. But increasing C_{ip} values with increasing temperature indicates that film diffusion is the rate-determining step of the sorption process of Zn^{+2} ions by DFZPC.

Table 2 : Kinetics model constants for Zn^{+2} ion sorption by DFZPC at different solution temperatures

Model	Zn^{+2} ion solution temperature (K)			
	289	298	303	313
q_{exp} (mg/g)	3.815	3.29	3.958	4.15
Pseudo-first-order model				
k_1(min^{-1})	0.001	0.014	0.016	0.017
q_e (mg/g)	3.668	3.291	3.029	3.018
R^2	0.96	0.72	0.515	0.466
Pseudo-second-order model				
k_2 (g/mg.min)	0.057	0.126	0.282	0.392
q_e (mg/g)	3.495	3.683	3.897	4.107
R^2	0.922	0.985	0.997	0.999
Weber and Morris intra-particle diffusion model				
K_i (mg/g min$^{0.5}$)	0.327	0.348	0.372	0.393
C_{ip} (mg/g)	-0.043	-0.001	0.021	0.029
R^2	0.976	1	0.995	0.993

3.3. Sorption isotherm

By fitting the equilibrium data to the sorption isotherm models, you can get the basic parameters for designing sorption systems. This is because the basic parameters tell you how much the sorbent can hold at the conditions of the system [38]. The most commonly used equilibrium isotherm models are:

i- The Langmuir isotherm model is used to explain monolayer adsorption on a sorbent's surface with a finite number of identical sorption sites. The Langmuir isotherm model in its linear form is given by Equation 6 [31]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{LM}} + \frac{1}{q_{LM}K_L} \tag{6}$$

Where q_{LM} is the maximum sorption capacity of the sorbent (mg/g), K_L is the Langmuir equilibrium constant (L/mg).

ii- The Freundlich isotherm model is used to describe non-ideal sorption on heterogeneous surfaces. The linear form of the Freundlich isotherm model is given by Equation 7 [39]:

$$lnq_e = lnK_F + \frac{1}{n}\ln C_e \tag{7}$$

Where K_F (mg/g)(mg/L)$^{-1/n}$ and n are the Freundlich constants.

iii- The Dubinin-Radushkevich (D-R) isotherm model is unlike the Langmuir isotherm model because it does not assume a homogeneous surface or a constant sorption potential. The D-R isotherm model in its linear form is given by Equation 8 [40]:

$$lnq_e = lnX_m - K_{DR}.\varepsilon^2 \tag{8}$$

where X_m is the maximum sorption capacity of the sorbent (mg/g), K_{DR} is an activity constant (mol^2/kJ^2) associated with the sorption energy, ε is the Polanyi potential (kJ/mol), which is mathematically equal to RT ln(1+1/C_e), and R is the universal gas constant in kJ/mol.K, T is the absolute temperature in K. The mean free energy E (kJ/mol) of sorption is calculated using Equation 9 [41]:

$$E = \frac{1}{\sqrt{2K_{DR}}} \tag{9}$$

iv- The Temkin isotherm model, contrasting the Langmuir and Freundlich isotherms, takes into consideration the interactions between sorbents, and metal ions to be sorbed and according to the concept of free sorption energy, it is a function of surface coverage [42]. The Temkin isotherm model in its linear form is given by Equation 10 [43]:

$$q_e = B_T \ln A_T + B_T \ln C_e \tag{10}$$

Where A_T (L/mg) is the constant of equilibrium binding and B_T = RT/b_T is a constant associated with the heat of sorption (mg/g) and b_T is the Temkin constant (kJ/mol).

The determined constants associated with the models are presented in Table ***3***. The results showed that the Langmuir isotherm model successfully described the sorption process by Equation 11.

$$\frac{C_e}{q_e} = \frac{C_e}{4.819\ \mathrm{mg/g}} + \frac{1}{4.819\ \mathrm{mg/g} * 0.108\ \mathrm{L/mg}} \tag{11}$$

This result can be explained by the fact that the sorption process of Zn^{+2} ions using DFZPC is derived from the formation of a monolayer of metal ions on the sorbent surfaces. In this case, such surfaces exhibit a finite number of homogeneous and uniform active sites [44,45]. Also, the Freundlich isotherm model represented the experimental data with a value of 1/n was < 1 which indicates $Zn+^2$ ions are favorably sorbed. The value of the mean sorption energy E was 0.845 kJ/mol (i.e., less than 8 kJ/mol) and the Temkin constant (b_T) value was 3.231 kJ/mol (i.e., less than 8 kJ/mol), which indicates the physical sorption of Zn^{+2} ions by DFZPC. The results of fitting with the Temkin model show that the removal of Zn^{+2} ions by DFZPC is an ion exchange mechanism dominating the adsorption mechanism. However, this conclusion is untrustworthy because of the low determination coefficient of this model and because more information about the adsorption mechanism is required to possibly elucidate the results [46].

Table 3: Sorption isotherm model constants for Zn^{+2} ions removed by DFZPC

Langmuir isotherm model				Freundlich isotherm model			
K_L (L/mg)	q_{LM} (mg/g)	R^2		K_F (mg/g)(mg/L)$^{-1/n}$	1/n	R^2	
0.108	4.819	0.932		0.948	0.326	0.798	
D-R isotherm model				Temkin isotherm model			
X_m (mg/g)	K_{DR} (mol^2/kJ^2)	E (kJ/mol)	R^2	A_T (L/mg)	B_T (mg/g)	b_T (kJ/mol)	R^2
3.592	1*10^{-6}	0.845	0.876	4.089	0.741	3.231	0.795

3.4. Thermodynamic parameters

The thermodynamic parameters, including the change in Gibbs free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were determined for Zn^{+2} ion sorption by DFZPC using Equations 12-15 [14,47]:

$$\Delta G° = \Delta H° - T\Delta S° \tag{12}$$

Where ΔG° can also be expressed as shown by Equation 13:

$$\Delta G° = -\mathrm{R\,T} \ln K_e^{\circ} \tag{13}$$

Substituting Equation 12 into Equation 13 gives the Van't Hoff equation, Equation 14:

$$\ln K_e^{\circ} = -\left(\frac{\Delta H°}{RT}\right) + \frac{\Delta S°}{R} \tag{14}$$

where K_e° is the thermodynamic equilibrium constant (dimensionless) that can be calculated using Equation 15 [48]:

$$K_e^{\circ} = \frac{K_L.1000.\ M.wt.[sorbate]°}{\gamma} \tag{15}$$

Where K_L represents the Langmuir equilibrium constant (L/mg), M.wt. represents the molar mass of sorbate, [sorbate]° represents the standard concentration of the sorbate, which is equal to 1 mol/L and ϒ is the activity coefficient (dimensionless). The values of ΔH° and ΔS° were determined from the intercept, and slope of the line plotted from ln K_e° versus 1/T. The thermodynamic parameters are presented in

Table 4. The small negative values of ΔG° indicate that the sorption process is spontaneous. It is found that the values of ΔG° became more negative as the temperature increased, demonstrating that high temperatures are more favorable for the sorption of Zn^{+2} ions by DFZPC. Similarly, the positive value of ΔH° indicates that the sorption process is endothermic. According to the literature [49], the sorption process is denoted as physical if the value of ΔH° is less than 84 kJ/mol and chemical if the ΔH° value ranges from 84 to 420 kJ/mol. The ΔH° value in this study was 4.813 kJ/mol confirming the physical nature of the sorption of Zn^{+2} ions by DFZPC. Finally, the positive value of ΔS° indicates increasing the randomness at the solid/solution interface during Zn^{+2} ion sorption. If the value of ΔS° is more than -10 J/mol. K, the sorption follows a dissociative mechanism; however, it follows an associative mechanism if the ΔS° value is less than -10 J/mol.K [50]. The ΔS° value in this study was 0.085 kJ/mol, which confirms that the sorption of Zn^{+2} ions by DFZPC involves a dissociative sorption mechanism.

Table 4: The calculated thermodynamic parameters for Zn^{+2} ions removed by DFZPC

Temperature °C (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol.K)
16 (289)	-19.841	4.813	0.085
25 (298)	-20.609		
30 (303)	-21.036		
40 (313)	-21.889		

3.5. Solidification by geopolymer

Table 5 shows the Zn^{+2} ion concentration leached from geopolymer-solidified spent DFZPC. The concentrations of ions leached from the geopolymer were found to be less than 1 mg/L (less than the permitted level). The geopolymerization technique effectively immobilizes harmful ions. However, it converts waste into a large volume of solids.

Table 5: Concentrations of Zn^{+2} ions leached into NaOH solution (0.05 M) from samples encapsulated with geopolymers

Time (week)	1	2	3	4	8	12
Zn^{+2} ion concentration (mg/L)	0.213	0.249	0.283	0.414	0.430	0.538

4. Conclusion

The green synthesis method used in this work allowed for the obtaining of a hierarchically porous zeolite-carbon composite from nanosized zeolite having low Si/Al without subjecting it to further thermal treatment, which was used in previous studies. This study revealed that the green porous composite was found to be a more cost-effective sorbent for the removal of Zn^{+2} ions from aqueous solutions. This composite combined ion exchange and adsorption properties (a dual-function composite), which allowed the physical sorption to occur via a chemical reaction. The maximum percent removal of Zn^{+2} ions 83% was achieved at a 6.4 pH solution, a 313 K solution temperature, and a 120 minutes contact time. Based on the sorption isotherm study, the Langmuir model exhibited the best fit to the experimental data of Zn^{+2} ion sorption by DFZPC. The sorption results' kinetics was fitted satisfactorily to the pseudo-second-order kinetic model and the Weber and Morris intra-particle diffusion rate kinetic model. The values of ΔG°, ΔH°, and ΔS° indicated that the sorption of the Zn^{+2} ions by DFZPC was a favorably spontaneous, endothermic, and dissociative mechanism. The obtained results revealed the potential of the DFZPC composite as a green porous composite for the remediation of toxic Zn^{+2} ions. In future studies, the DFZPC composite can be examined as a sorbent for the removal of other heavy metal ions from aqueous solutions.

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