Two–three parameters isotherm modeling, kinetics with statistical validity, desorption and thermodynamic studies of adsorption of Cu(II) ions onto zerovalent iron nanoparticles

Adewumi O. Dada¹6,7*, Folahan A. Adekola², Ezekiel O. Odebunmi³, Adeniyi S. Ogunlaja⁴ & Olugbenga S. Bello¹5

Adsorption of problematic copper ions as one of the endocrine disruptive substances from aqueous solution onto nanoscale zerovalent iron (nZVI) was studied. The high pore size 186.9268 Å, pore diameter 240.753 Å, and BET surface area 20.8643 m² g⁻¹ and pH(pzc) enlisted nZVI as an efficient nano-adsorbent for treatment of heavy metals from synthetic wastewater. SEM and EDX revealed the morphology and elemental distribution before and after adsorption. 98.31% removal efficiency was achieved at optimum adsorption operational parameters. Of all the thirteen isotherm models, equilibrium data were well fitted to Langmuir. Kinetics and mechanism data across the concentrations from 10 to 200 mg L⁻¹ were analyzed by ten models. PSO best described kinetics data as confirmed by various statistical error validity models. The intraparticle diffusion model described that the intraparticle diffusion was not the only rate-limiting step. The adsorption mechanism was diffusion governed established by Bangham and Boyd models. Feasible, spontaneous, endothermic, and degree of randomness were reveal by the thermodynamic studies. Better desorption index and efficiency were obtained using HCl suggesting multiple mechanism processes. The performance of ZVI suggested it has a great potential for effective removal of endocrine disruptive cationic contaminant from wastewater.

Endocrine disruptive compounds (EDC) have been among emerging contaminants whose adverse effects in the environments have received the attention of various researchers. Heavy metal ions have been identified to have hazardous effects on the endocrine system. Copper, as heavy metal ions, has been listed among endocrine disruptive compounds. Some of the endocrine disruptive effects of copper ions are: Increased levels of plasma cortisol associated with protein synthesis, cell proliferation, and apoptose in gill cells. It can also lead to an increase in Catecholamines which promotes metabolic and haematopoietic responses¹². Several anthropogenic activities and natural phenomena release copper ions into the environment.³ The largest threat to human lives and aquatic organisms arises from the soluble form of copper.¹ These soluble copper ions get released into the environment via different agricultural applications. Research has shown that high uptakes of copper may cause liver and kidney damage and even death.⁵–⁷. Research on the utilization of nanoparticles is on the increase due to their special characteristics. Nanotechnology is a trending research area for the science and technology of

¹Nanotechnology Laboratory, Industrial Chemistry Programme, Department of Physical Sciences, Landmark University, P.M.B.1001, Omu-Aran, Kwara State, Nigeria. ²Department of Industrial Chemistry, University of Ilorin, P.M.B. 1515, Ilorin, Nigeria. ³Department of Chemistry, University of Ilorin, P.M.B. 1515, Ilorin, Nigeria. ⁴Department of Chemistry, Nelson Mandela Metropolitan University, P.O. Box 77000, Port Elizabeth 6031, South Africa. ⁵Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology, P.M.B 4000, Ogbomosho, Oyo State, Nigeria. ⁶Landmark University, Sustainable Development Goal (SDG) Group 6: Clean Water and Sanitation, Omu-Aran, Nigeria. ⁷Landmark University, Sustainable Development Goal (SDG) Group 11: Sustainable Cities and Communities, Omu-Aran, Nigeria. ²email: dada.oluwasogo@lmu.edu.ng
functional structures at the molecular scale. This covers current research work in chemical, physical, biological, medical, material sciences, and engineering. Nano-materials have been reported to be applicable in environmental remediation, catalysis, development of optical devices, and medicine. Nanoparticles are the new trend of effective adsorbents used in the decontamination of water and immobilization of heavy metal ions from their solutions. A study conducted by the US Environmental Protection Agency showed that zerovalent iron nanoparticle (nZVI) is environmentally benign and effective in soil and water remediation. nZVI has found relevance in the adsorption of problematic toxicants such as EDC heavy metal ions. Of all various conventional approaches described for heavy metal ions removal, adsorption via adsorption is much more favored since it is low cost, efficient, available, and easy to operation.

The most vital quantity for comprehending the adsorption process is gotten from adsorption isotherm models. The parameters of isotherm modeling are essential factors relevant to the design of an effluent treatment reactor. More so, extensive isotherm models were investigated to predict and compare adsorption performances. Most common isotherm models are Langmuir and Freundlich, Temkin and Dubiniv–Kaganer–Raduskevich (DKR). Other isotherm models used in this study are Halsey, Jovanovic, Elovich, Jossen, Flory–Huggins, Kissel, Harkins–Jura, Fowler–Guggenheim, and Redlich–Peterson. In most adsorption studies carried out using nZVI, no detailed investigation has been reported for mathematical isotherm parameters that could be utilized for treatment reactor design. This has not been given a priority hence a research gap of global interest has been created. The energy of the adsorption process for uptake of endocrine disruptive copper ions via thermodynamic studies was examined to determine the feasibility, spontaneity, energy content, and degree of disorderliness of the process. More so, the mechanism vis-à-vis desorption studies were investigated using three desorbing agents. The reality of the adsorption process was assessed by post-adsorption characterization using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray (EDX).

Materials and methods
All through this work, analytical grade reagents were used without further purification. Double-Distilled-Deionized water, Copper sulphate (CuSO₄·5H₂O, Breckland Scientific Batch No. 6688), Isopropyl alcohol (BDH, Min. Assay 99%, Prd No. 29694 6). Other chemicals purchased from Sigma Aldrich, USA are Sodium borohydride (NaBH₄), Iron (III) chloride (FeCl₃·6H₂O), Hydrochloric acid (HCl), Sodium hydroxide (NaOH), Sodium nitrate (NaNO₃).

Synthesis of zerovalent iron nanoparticles (nZVI). The synthesis of nZVI for the removal of endocrine disruptive heavy metal ions was undertaken by following the procedure described in our prior studies. Under an anaerobic environment, a resulting black coloration of core–shell zerovalent iron nanoparticles (nZVI) was obtained from the reaction between 0.023 M solution of FeCl₃·6H₂O and 0.125 M solution of NaBH₄ in ratio 1:5. Detailed synthetic procedure is presented in the supplementary document associated with this study. The synthesis equation is depicted in Eq. (1):

\[
4\text{Fe}^{3+} + 3\text{BH}_4^- + 9\text{H}_2\text{O} \rightarrow 4\text{Fe}^{0} \downarrow + 3\text{H}_2\text{BO}_3^- + 12\text{H}^+ + 6\text{H}_2 \uparrow
\]  

(1)

Surface charge (pH_{pzc}), BET surface area, surface morphology and elemental distribution. Following the salt addition and pH variation method, the point of zero charge was determined as presented in the supplementary materials. Surface area by BET, pore width, and volume were determined using Micrometrics AutoChem II Chemisorption Analyzer. The surface morphological characterization and elemental analysis were carried out using a Scanning Electron Microscopy (SEM) integrated with Energy Dispersive X-ray (EDX) analyzer. SEM images and EDX spectra were obtained using a TESCAN Vega TS 5136LM typically at 20 kV at a working distance of 20 mm. Samples for SEM analysis were prepared by coating them in gold using a Balzers’ Sputtering device.

Effect of stirring speed, pH, and co-existing ions. In order to optimize the stirring speed, 160–240 rpm speed was studied at optimum conditions. Effect of pH was studied by regulating the solution to the desired pH value using 0.1 M NaOH and 0.1 M HNO₃ solutions. Effect of Co-existing ions/Ionic strength varying the concentration of NaCl introduced into Cu²⁺ solution from 0.001 to 1.0 M.

Batch isotherm, kinetics, and thermodynamic studies. A typical batch adsorption study was carried out following procedure reported in our previous study. 1000 ppm Cu²⁺ stock solution was prepared by dissolving 2.5 g of CuSO₄·5H₂O in 1000 mL of distilled-deionized water. Study on initial Cu²⁺ ion concentration was examined by adding 100 mg nZVI at different Cu (II) ions concentrations (10–200 ppm) and residual concentration determined by using AAS model AA320N. The quantity adsorbed and percentage removal efficiency were calculated utilizing Eqs. (2) and (3):

\[
Q = \frac{(c_0 - c_e)V}{m}
\]  

(2)

\[
% \text{RE} = \frac{C_i - C_e}{C_i} \times 100
\]  

(3)
The characteristics and mechanism of the adsorption process were investigated from the study of the Ce-dependent changes of $Q_e$ applied to thirteen isotherm models. Similarly, the batch adsorption kinetic experiments were conducted at optimum conditions for contact time ranging from 10 to 120 min. Adsorption capacities at contact time were obtained using Eq. (4):

$$Q_t = \frac{(C_0 - C_e)V}{W}$$  \hspace{1cm} (4)

Kinetic data were fitted to ten kinetics and mechanism models.

From the thermodynamics studies, the effect of temperature at optimum conditions was investigated at five different temperatures (298 K, 303 K, 318 K, 328 K, 333 K) for adsorption of endocrine disruptive Cu$^{2+}$ onto nZVI following our previously reported procedure.\textsuperscript{24,25} The study was carried out in a temperature-controlled water bath. Data obtained were fitted to Van’t Hoff equation depicted in Eqs. (5) and (6).

$$\log K_c = \frac{-\Delta S^o}{2.303R} - \frac{\Delta H^o}{2.303RT}$$  \hspace{1cm} (5)

$$\Delta G = -2.303RT \log K_c$$  \hspace{1cm} (6)

R is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), T the absolute temperature (K), $K_c$ ($q_e/C_e$) an equilibrium constant at various temperature. Standard enthalpy change $\Delta H^o$ (kJ mol$^{-1}$) and standard entropy change $\Delta S^o$ (J mol$^{-1}$ K$^{-1}$) were determined from the slope and intercept of the Van’t Hoff plot of $\log K_c$ versus $1/T$\textsuperscript{26,27}.

Desorption studies. The desorption is a means of regenerating the adsorbent capacity for reusability and cost effectiveness determination. Desorption studies were investigated using the following eluents: deionized (DI) water, 0.2 M HCl and 0.2 M CH$_3$COOH, at pre-determined optimum conditions. The desorption capacity, percentage desorbed, desorption efficiency and desorption index were determined using Eqs. (7)–(10):

$$q_{des} = \frac{C_{des}V}{W}$$  \hspace{1cm} (7)

$$\% \text{ Desorption} = \frac{C_{des}}{C_i} \times 100$$  \hspace{1cm} (8)

$$\% \text{ Desorption Efficiency} = \frac{q_{des}}{q_e} \times 100$$  \hspace{1cm} (9)

$$\text{Desorption index} = \frac{\% \text{ total metal removed after adsorption}}{\% \text{ total metal remained on the adsorbent after desorption}}$$  \hspace{1cm} (10)

where $q_{des}$ is the quantity of metal ion desorbed (mg g$^{-1}$), $q_e$ is the quantity of metal adsorbed after sorption (mg g$^{-1}$), $C_{des}$ is the concentration of metal ion left after desorption (mg L$^{-1}$), V is the volume of the metal ion solution (mL) while W is the weight of adsorbents (mg).

Results and discussion
nZVI physicochemical characterization: pH(pzc), BET surface area, pore volume and pore size. Summarized in Table 1 are pH, point of zero charge (PZC), BET surface area, and other physicochemical parameters describing the core–shell. The point of zero charge finds relevance in surface and nanoscience. Figure S1 (from the supplementary document associated with this study) shows the pH(pzc) of nZVI. It revealed that adsorption of Cu$^{2+}$ would take place at a pH > pH$_{pzc}$ as a result of more active binding being available due to deprotonation and low electrostatic repulsion. This finding shows that nZVI was positive at pH < pH$_{pzc}$ and negative at pH > pH$_{pzc}$. Thus this signposts the suitability of nZVI for effective adsorption. The BET surface area 20.86 m$^2$ g$^{-1}$ and the external surface area 16.4503 m$^2$ g$^{-1}$ being greater than their corresponding micropores further support the suitability of nZVI for adsorption. Higher surface area enhances the adsorption process as supported. Therefore, it can be deduced that nZVI nano-adsorbent would utilize its external surfaces for heavy metal uptake than its micropore areas\textsuperscript{29}.

SEM/EDX characterization. Percolation of EDC-Cu$^{2+}$ into the pores ad matrix of nZVI was proved by the SEM/EDX depicted in Fig. 1A–D. Figure 1A revealed the SEM image before adsorption while Fig. 1B depicted the EDX with an intense peak of a zerovalent iron nanoparticle. Before adsorption spherical, chain-like aggregated morphology of nZVI was revealed SEM. The core–shell nature of zerovalent iron with intense peaks between 0.6–6.4 and 7.0 keV was revealed from the EDX result in Fig. 1B. Presented in Fig. 1C is the SEM micrograph showing swollen and robust nature of the surface of the nZVI nano-adsorbent after adsorption suggesting that the nZVI surface had been Cu-loaded up. More so, corroborating the result from SEM, Fig. 1D revealed the EDX spectrum showing the presence of Cu(II) as evidence of Cu adsorption onto core–shell nZVI. This is supported by finding in the literature\textsuperscript{30}. 


Effect of operational parameters. Effect of initial Cu\textsuperscript{2+} concentration. A major role in the adsorption study is played by the factor of initial concentration at optimum conditions presented in supplementary document as seen in Figure S2. This showed that at optimum conditions, 85.04% RE and 81.04 mg g\textsuperscript{-1} quantity of Cu\textsuperscript{2+} was adsorbed. The extent of removal of Cu(II) ion cation increased based on the availability of more active sites at lower concentrations until the pore sizes were saturated at an advanced concentration (150–200 mg L\textsuperscript{-1}).

| Physicochemical parameters | nZVI                   |
|----------------------------|------------------------|
| pH                         | 6.80                   |
| PZC                        | 5.84                   |
| BET surface area           | 20.8643 m\textsuperscript{2} g\textsuperscript{-1} |
| t-Plot micropore area      | 4.4140 m\textsuperscript{2} g\textsuperscript{-1} |
| t-plot external surface area | 16.4503 m\textsuperscript{2} g\textsuperscript{-1} |
| BJH adsorption cumulative surface area of pores | 19.120 m\textsuperscript{2} g\textsuperscript{-1} |

| Pore volume                |
|----------------------------|
| Single point adsorption total pore volume of pores | |
| less than 1103.48 Å diameter at P/P\textsubscript{0} = 0.982136052: | 0.097502 cm\textsuperscript{3} g\textsuperscript{-1} |
| t-Plot micropore volume: | 0.001895 cm\textsuperscript{3} g\textsuperscript{-1} |
| BJH adsorption cumulative volume of pores | 0.115083 cm\textsuperscript{3} g\textsuperscript{-1} |

| Pore size                  |
|----------------------------|
| Adsorption average pore width (4 V/A by BET): | 186.9268 Å |
| BJH Adsorption average pore diameter (4 V/A): | 240.753 Å |

Table 1. Physicochemical parameters of nZVI.

Figure 1. (A) SEM micrograph of nZVI before adsorption. (B) EDX spectrum of nZVI before adsorption. (C) SEM micrograph of Cu-loaded-nZVI after adsorption. (D) EDX of Cu-loaded-nZVI after adsorption.
Concentration gradient was built up in the Cu-nZVI system due to intensification of drive force as concentration increased from 10 to 200 mg L\(^{-1}\). This is supported by the findings in the literature\(^1\).

Effect of contact time. The build-up of Cu(II) ions at the solid–liquid interfaces are controlled by the contact time. From this study, optimization of the contact time was investigated from 10 to 120 min. Fast kinetics from the bulk to the outer and inner surface of the nano-material (nZVI) identified by a short contact time to reach equilibrium was observed in the supplementary document as seen in Figure S3 Quantity of Cu(II) adsorbed increase from 4.96 to 82.82 mg g\(^{-1}\) as the initial Cu\(^{2+}\) concentration increased from 10 to 200 ppm. A similar trend was observed by Baby et al.\(^{26}\) on the adsorption of heavy metals.

Effect of initial solution pH. The key to the adsorption of heavy metal ions is the solution pH because it affects the surface chemistry of the system. A plot of the effect of initial concentration is presented in the supplementary document as seen in Figure S4 portrayed the effect of pH at optimum conditions. Coined from the understanding of the isoelectric point of the pH(pzc), nZVI is suitable for the uptake of cationic pollutants such as Cu\(^{2+}\) since the pH > pH(pzc). At low solution pH, the system is protonated leading to electrostatic competition among Cu\(^{2+}\) and other cationic species such as H\(^{+}\), Cu(OH)\(^{+}\), Cu(OH)\(_2\). However, at solution pH > pH(pzc), the system is negative, deprotonation occurs, there is less competition between Cu\(^{2+}\) and other anionic species (Cu(OH))\(_{-}\) and Cu(OH))\(_{-}\)\(^{-}\). Effective adsorption occurs at pH > pH(pzc). Optimum adsorption was achieved at pH 6 with 98.31% removal efficiency and quantity adsorbed 73.73 mg g\(^{-1}\) indicating effective binding of Cu\(^{2+}\) onto nZVI surface. This is corroborated by the findings of other researchers\(^{35}\).

Effect of ionic strength. Analysis of Figure S5 (presented in the supplementary document associated with this study) showed the effect of ionic strength on Cu\(^{2+}\) adsorption. Pollution of the water system is not limited to heavy metal ions only, some co-existing ions increase the salinity and ionic strength of the water body as investigated in this study. Co-existing ions polluted waste system increases the salinity and background electrolyte of the water body. A decrease in the percentage of Cu\(^{2+}\) removed from 81.99 to 79.73% with a reduction in quantity adsorbed from 61.49 to 59.79 mg g\(^{-1}\) was observed in Figure S5. The decrease in Cu(II) ions uptake may also be due to a decrease in the electrostatic attraction arising from compressed electrical diffuse double layer supporting the findings of Advantageously, the removal efficiency of 81.99% shows that nZVI is an effective nano-sorbent in treatment industrial discharge containing co-existing ions. This is supported by findings in the literature\(^{22}\).

Effect of stirring speed. This study demonstrated as shown in Figure S6 (supplementary document) that at 200 rpm maximum adsorption of Cu\(^{2+}\) onto nZVI was attained. Stirring speed is also one of the important parameters in adsorption studies because it promotes turbulence, frequency of collision and improves mass transfer in the medium between the two phases. At 200 rpm, the percentage Cu\(^{2+}\) removal efficiency and quantities adsorbed are 96.98% and 72.73 mg g\(^{-1}\) for nZVI. Stirring speed increases the retention of Cu\(^{2+}\) and it encourages a better transfer of Cu\(^{2+}\) between solid–liquid interfaces (Cu\(^{2+}\)-nZVI system)\(^{18}\). No appreciable percentage removal efficiency was observed after 200 rpm and all other study was carried out at this stirring speed.

Two–three parameters adsorption isotherm modelings. One of the important and significant aspects of adsorption studies is mathematical isotherm modeling. Isotherm modeling is important in order to observe the relationship between nZVI and Endocrine disruptive Cu(II) ions at equilibrium conditions. A good understanding of this would significantly enhance the design of the adsorption system, effluent treatment reactor, and the pattern describing adsorbate-adsorbent interaction. Equilibrium data obtained from initial concentration were analyzed using thirteen mathematical isotherm models. All mathematical isotherm models used in this study were presented in Table 2 together with their non-linear, linear equations and parameters’ description. The estimated parameters are portrayed in Table 3. The plots in the isotherm studies are presented in the supplementary document associated with this article from Figure S7A–S7M.

Langmuir isotherm model (Figure S7A) assumes no interaction of the neighboring sites, monolayer surface, identical active sites, uniformity in adsorption energy\(^{1}\). The non-linear and linear Langmuir equations are presented in Eq. (11). In this study, the Langmuir isotherm model has the highest correlation coefficient \((R^2 > 0.97)\) indicating the appropriateness and best fitting of equilibrium data to the Langmuir model. The Langmuir essential feature, as well as the separation factor or dimensionless constant \((R_L)\), was calculated using Eq. (12)\(^{20}\). Values of \(R_L\) portrayed in Table 3

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the Freundlich isotherm model. However, the negative value of n_F, couple with the low R² value of Harkin–Jura (Eq. 19, Figure S7F) showed that the adsorption nature of the nZVI surface is not multilayer and heterogeneous.38

Combination of both the Langmuir and Freundlich isotherm attribute could be assessed in Redlich–Peterson isotherm model (Eq. 20, Figure S7G). Redlich–Peterson correlation value (R² = 0.9475) shows its versatility and fitting to equilibrium data.42 Figure S7H depicts the Jovanovic isotherm model (Eq. 21) plot model. Jovanovic isotherm model corresponds to another approximation for monolayer localized adsorption without considering the surface coverage (θ) of the adsorbate on the nZVI. Jovanovic isotherm model corresponds to another approximation for monolayer localized adsorption without considering the surface coverage (θ) of the adsorbate on the nZVI.

| Types of adsorption models | Non-linear expression | Linear expression | Parameters nomenclature and description |
|----------------------------|-----------------------|------------------|-----------------------------------------|
| Langmuir                  | \( Q_e = \frac{Q_{\text{max}}K_L C_e}{1 + K_L C_e} \) | \( \frac{C_e}{Q_e} = \frac{C_e}{Q_{\text{max}}} + \frac{1}{K_L} \) | \( K_L \) is the Langmuir isotherm constant (L mg⁻¹) related to the binding energy of adsorption. \( Q_{\text{max}} \) is the maximum monolayer coverage capacity (mg g⁻¹). \( R_L \) is dimensionless separation factor indicating the nature and favourability of adsorption process. From slope and intercept of linear plot of Ce/Qe versus Ce, \( K_L \) and \( Q_{\text{max}} \) were determined. |
| Freundlich                | \( Q_e = K_F C_e \) | \( \log Q_e = \log K_F + \frac{1}{n_F} \log C_e \) | \( K_F \) is Freundlich indicator of adsorption capacity. \( n_F \) is a slope of the linear plot of log Qe versus log Ce. |
| Temkin                    | \( Q_e = \frac{bT}{R T} \ln(A_t C_e) \) | \( Q_e = \frac{bT}{R T} \ln(A_t) + \frac{bT}{R T} \ln C_e \) | \( b_T \) is the Temkin isotherm constant related to the heat of adsorption and \( A_t \) is the Temkin equilibrium binding constant (L g⁻¹). \( R \) is universal gas constant (8.314 J mol⁻¹ K⁻¹). \( T \) is absolute Temperature in Kelvin. \( B = R T/b_T \) is constant related to heat of sorption (J mol⁻¹) obtained either from intercept or slope. |
| DKR                       | \( Q_e = Q_{\text{DKR}} \exp^{-A_{DKR} \cdot e^{2}} \) | \( \ell_n_0 \) = \( \ell m Q_{\text{DKR}} - A_{DKR} \ell^2 \) \( \ell = \frac{R T n (1 + \frac{1}{\ell})}{E} \) | \( \ell_n_0 \) is the theoretical adsorption isotherm saturation capacity (mg g⁻¹) obtained from intercept. \( A_{DKR} \) is the D–R isotherm constant (mol² kJ⁻²) related to free sorption energy obtained from the slope. E is Polanyi potential determined by the expression \( E = R T \ln (1 + 1/\ell_n) \). E is the mean adsorption free energy helpful in determining the adsorption nature (phy- or chemisorption of the adsorption process). \( Q_{\text{DKR}} \) and \( A_{DKR} \) were determined from intercept and slope of linear plot of ln qe versus \( E^2 \). |
| Halsey                    | \( Q_e = \exp \left[ \frac{\ln(K_H \cdot \theta)}{n_F} \right] \) | \( \log Q_e = \left( \frac{1}{n_F} \right) \ln(K_H) - \left( \frac{1}{n_F} \right) \ln C_e \) | \( K_H \) is Halsey isotherm constant; \( n_F \) is the Halsey isotherm exponent. Both were determined from linear plot of logQe versus log Ce. |
| Kisselev                  | \( Q_e = \frac{Q_{\text{max}}}{1 - \theta} \) | \( \ln \left( \frac{Q_e}{Q_{\text{max}}} \right) = \ln K_i + 1/Q_{\text{max}} \) | \( K_i \) is Kiselev equilibrium constant (L g⁻¹). \( Q_{\text{max}} \) is the Temkin isotherm equilibrium binding constant (L g⁻¹) related to the heat of adsorption and \( K_i \) is equilibrium constant related to free sorption energy obtained from the slope. E is Polanyi potential determined by the expression \( E = R T \ln (1 + 1/\ell_n) \). E is the mean adsorption free energy helpful in determining the adsorption nature (phy- or chemisorption of the adsorption process). \( Q_{\text{DKR}} \) and \( A_{DKR} \) were determined from intercept and slope of linear plot of ln qe versus \( E^2 \). |
| Jossen                    | \( C_e = \frac{Q_{\text{max}}}{\theta} \exp \left( F_i \theta \right) \) | \( \ln \left( \frac{C_e}{Q_{\text{max}}} \right) = -\ln H_j + F_i Q_{\text{θ}} \) | \( H_j \) is Jossens isotherm constant (it corresponds to Henry’s constant) related to isotherm constant and it is characteristic of the adsorbent irrespectively of temperature and the nature of adsorbents, and \( F_i \) is Jossens isotherm exponent. H and F depend only on temperature. |
| Flory–Huggins             | \( C_e = K_F H (1 - \theta) \cdot Q_{\text{θ}} \) | \( \log \left( \frac{C_e}{Q_{\text{max}}} \right) = \log K_F + n_H \log (1 - \theta) \) | \( K_F \) is Flory–Huggins equilibrium constant (L mg⁻¹). \( n_H \) is degree of surface coverage. \( n_H \) is number of adsorbates occupying adsorption sites, and \( K_F \) is Flory–Huggins equilibrium constant (L mol⁻²). \( n_H \) and \( K_F \) were determined from the linear plot of Log(Q/ads) versus Log(1 - θ). |
| Fowler–Guggenheim         | \( K_F C_e = \frac{n_H}{Q_{\text{θ}}} \exp \left( \frac{20 H_i}{T} \right) \) | \( \ln \left( \frac{C_e}{Q_{\text{max}}} \right) = -n_H K_F + \frac{20 H_i}{T} \) | \( K_F \) is the Fowler–Guggenheim (F–G) equilibrium constant (L mg⁻¹). \( θ \) is the fractional coverage, R is the universal gas constant (kJ mol⁻¹ K⁻¹), \( T \) is the temperature (K), and W is the interaction energy between adsorbed molecules (k cal mol⁻¹). \( K_F \) and \( W \) were determined from the linear plot of ln(Ce/Qe) versus θ. |

Table 2. Adsorption isotherm and kinetics models35,43.47.


lateral interactions which ought to be similar to the Langmuir isotherm model. However, a lower correlation coefficient \((R^2 = 0.6105)\) obtained in this study indicated that there is a lateral interaction and thus this model lower approach towards saturated compared to Langmuir adsorption isotherm as reported by Al-Ghouti et al.\(^44\). This is supported by the fit and parameters obtained from Fowler–Guggenheim (F–G) isotherm model (Eq. 27, Figure S7M). Taken into consideration is the lateral interaction of adsorption of EDC-Cu\(^{2+}\) onto nZVI by the FG- isotherm model\(^45\). As reported by the literature, the interaction between the adsorbed molecule is attractive, if \(W\) is positive; repulsive interaction if \(W\) is negative and no interaction between the adsorbed molecules will be observed if \(W = 0\)\(^42,46\). In this study, the fit of the Fowler–Guggenheim isotherm model (\(R^2 = 0.9487\)) and positive value of \(W\) (\(W = 881.02 \text{ J mol}^{-1}\)) indicated that there is positive contact in the Cu\(^{2+}\)-nZVI system, hence the adsorption heat increased with loading confirming endothermic adsorption process as observed in the thermodynamics studies.

The screening and arrangement are based on the understanding of the important parameters \((Q_{\text{max}}\) and \(R^2\)). With regards to \(Q_{\text{max}}\) (in descending order) Langmuir > DKR > Elovich > Jovanovic. With respect to \(R^2\) (in descending order): Langmuir > Jossen = Elovich > Freundlich = Halsey > Temkin > Fowler–Guggenheim > Jovanovic. Presented in Table 4 is the comparison of maximum monolayer adsorption capacities of adsorption of Cu\(^{2+}\) onto various nano-adsorbents and nZVI used in this study. It is obvious that nZVI exceedingly surpassed other existing adsorbents reported. This indicated that nZVI is an excellent potential nano-adsorbent for effective removal of endocrine disruptive heavy metal ions.

**Adsorption kinetic with statistical error validity modeling.** A kinetic study was undertaken to understand the controlling pathway, the rate of surface adsorption of the contaminant to the adsorbent, and the

| S. no. | Adsorbents | Adsorption capacity \((Q_{\text{max}})\) (mg/g) | References |
|-------|------------|---------------------------------|-----------|
| 1     | Pectin-iron oxide | 48.99 | \(^38\) |
| 2     | Chitosan-bound Fe\(_3\)O\(_4\) magnetic nanoparticles | 21.5 | \(^39\) |
| 3     | Aminated polyacrylonitrile nanofiber mats | 30.40 | \(^29\) |
| 4     | Carbon nanotubes | 24.49 | \(^39\) |
| 5     | Carboxymethyl-β-cyclodextrinconjugated magnetic nanoparticles | 47.29 | \(^42\) |
| 6     | Fe\(_3\)O\(_4\) magnetic nanoparticles coated with humic acid | 46.3 | \(^43\) |
| 7     | Magnetic gamma-Fe\(_3\)O\(_4\) nanoparticles coated with poly-l-cysteine | 42.9 | \(^40\) |
| 8     | Magnetic nano-adsorbent modified by gum Arabic | 38.5 | \(^40\) |
| 9     | Hydroxyapatite nanoparticles | 36.9 | \(^40\) |
| 10    | Maghemite nanoparticle | 27.7 | \(^40\) |
| 11    | Amino-functionalized magnetic nanosorbent | 25.77 | \(^40\) |
| 12    | Poly(hydroxethyl methacrylate) | 58.0 | \(^40\) |
| 13    | Fe\(_3\)O\(_4\) nanoparticle | 37.04 | \(^10\) |
| 14    | Fe\(_3\)O\(_4\) nanoparticle | 19.61 | \(^51\) |
| 15    | nZVI | 90.09 | This present study |

**Table 4.** Comparison of adsorption capacity nZVI other nano-adsorbents used for Cu\(^{2+}\) removal.
quantity of the adsorption capacity. The kinetics equations vis-à-vis pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich, Avrami, and Power Function (Fractional power) are represented on Eqs. (28)–(34).

\[
\text{Pseudo first-order (Lagren's rate equation)} \quad \ell \log(q_e - q_t) = \ell \log(q_e) - \frac{k_1 t}{2.303} (28)
\]

\[
h_1 \text{ initial pseudo first-order adsorption rate (mg g}^{-1} \text{ min}^{-1}) \quad h_1 = k_1 q_e (29)
\]

\[
\text{Pseudo second-order rate equation:} \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t (30)
\]

\[
h_2 \text{ is the initial pseudo second-order adsorption rate:} \quad h_2 = k_2 q_e^2 (31)
\]

\[
\text{Elovich model:} \quad q_t = \frac{1}{\beta} \ell n(\alpha \beta) + \frac{1}{\beta} \ell n(t) (32)
\]

\[
\text{Avrami model:} \quad \ln \left( \ln \left( \frac{q_e}{q_e - q_t} \right) \right) = n \ln k_{AV} + n \ln t (33)
\]

\[
\text{Power Function:} \quad \ell \log(q_t) = \log(k) + v \log(t) (34)
\]

The kinetic plots are presented in Fig. 2A–E with error bars indicating the application of error models and the evaluated parameters are presented in Table 5. The kinetic constant \(k\) of Pseudo first order (PFO), its adsorption rate constant \(h_1\), disagreement between \(q_{e, \text{exp}}\) and \(q_{e, \text{cal}}\) and low correlation coefficient, \(R^2 < 0.90\), demonstrated that PFO is not applicable in this study. A similar low trend in the \(R^2\) value was observed in the Avrami model demonstrating that it is not applicable in this study. A good agreement between the experimental quantity adsorbed (\(q_{e, \text{exp}}\)) and the calculated quantity adsorbed (\(q_{e, \text{cal}}\)) was observed in PSO, Elovich, and Power function. From the Elovich model, the values of \(\alpha\) (adsorption rate) increased with an increase in concentration as a result of an increase in the number of sites. The values of \(1/\beta\) at 10 ppm, 50 ppm, 100 ppm, and 150 ppm are 5.882, 11.764, and 17.123 respectively. These values reflect the number of sites available for adsorption. Kinetic parameters from Power Function in Table 5 indicated time-dependent of Cu(II) onto nZVI with the value of constant \(v\) less than 1 across all the concentrations. Of all these kinetic models, PSO best described the Cu(II) adsorption process and this was supported by the statistical error validity model presented in Table 5. The PSO initial adsorption rate \(h_1\) increases with increase in concentration from 33.67 to 238.095 mg g\(^{-1}\) min\(^{-1}\). \(R^2\) values range from 0.99 to unity demonstrating the best fitting by PSO suggesting chemisorption mechanism.

**Statistical validity of the kinetic models.** Assessment on the best kinetic fitting model that is always based on linear regression coefficient could be biased inherent, hence the need for statistical validity model. The suitability, agreement, and best fit among the kinetic models are judged not only by regression coefficient \(R^2\) but also with the use of statistical error validity models. Validity of kinetic data was fitted to statistical error validity models namely: Average relative error (ARE), Normalized Standard Deviation \(\Delta q\) (%), Hybrid fractional error function (HYBRD), Derivative of Marquardt’s percent standard deviation (MPSD), Standard deviation of relative Error (SRE). The various statistical functions are presented in Table 6. Presented in Table 7 are the statistical error validity data of the kinetic models. Five statistical tools were used for the validity of these kinetic models. It is observed that the closer the agreement between the experimental quantity adsorbed (\(q_e, \text{exp}\)) and the calculated quantity adsorbed (\(q_e, \text{cal}\)), the lower the values of these statistical tools, the better the model. In order to justify and juxtapose the best model, a reference was made to the coefficient of regression \(R^2\). The higher the \(R^2\) values, the closer the values of \(q_e, \text{exp}\), and \(q_e, \text{cal}\), the lower the values of \(\Delta q, HYBRD, MPSD, ARE,\) and \(SRE\), the better the kinetic models in describing the sorption process. The values in Table 4 vividly show that pseudo-second-order at various initial Cu\(^{2+}\) concentrations (10 ppm, 50 ppm, 100 ppm, 150 ppm, and 200 ppm) best describe the sorption process. The model can be arranged in descending order with respect to \(R^2\): pseudo-second-order > Elovich > fractional power > Avrami > pseudo-first-order.

**Adsorption mechanisms for sorption of Cu\(^{2+}\) onto nanoscaled zerovalent iron (nZVI).** Figure 3A–E show the linear plots of intraparticle diffusion, liquid diffusion, external diffusion, Bangham and Boyd models. Adequate understanding of the adsorption mechanism is enhanced by the determination of the rate-controlling/determining step. The three definite steps that could be used to describe the adsorption rate are (1): Intraparticle or pore diffusion, where adsorbate molecules percolate into the interior of adsorbent particles, (2) Liquid film or surface diffusion where the adsorbate is transported from the bulk solution to the external surface of the adsorbent, and (3) adsorption on the interior sites of the sorbent. Since the plot of Intraparticle diffusion (Fig. 3A) did not pass through the origin, it is demonstrated that it is not the only rate-determining step. Other mechanisms such as surface diffusion and external diffusion also participated in the mechanism of Cu(II) removal. However, the higher \(R^2\) values of intraparticle diffusion from the evaluated parameters presented in Table 8 demonstrated that the mechanism is pore diffusion dependent which was confirmed by Bangham and scattered plot of Boyd models. The intercept of intraparticle diffusion which is the thickness of the
The surface gives information about the contribution of the surface sorption in the rate-determining step. The larger the intercept, the greater the contribution of nZVI in adsorption of Cu²⁺ as observed from the trend across the concentrations investigated.

**Thermodynamics analysis.** Thermodynamics analysis is imperative to determine the (enthalpy change) heat content (ΔH); entropy change (degree of randomness, ΔS), possibility, and spontaneity (Gibbs free energy change, ΔG) in every adsorption process. The plots in thermodynamics studies are presented in the supplementary document associated with this article. As observed in Figure S8, intensification in the percentage removal efficiency was attained with an increase in temperature of the system supporting the endothermic process. This is due to a decrease in the mass transfer resistance and boundary layer thickness of nZVI. Van’t Hoff’s linear plot of log Kc against 1/T was portrayed in Figure S9 and the result obtained was presented in Table 9. The positive value of ΔH (+50.6059 kJ mol⁻¹) confirmed that the adsorption process is endothermic in nature. The positive value of ΔS (+174.679 J mol⁻¹ K⁻¹) shows an increase in the degree of randomness of the lateral interaction during the adsorption of Cu²⁺ at the solid/liquid interface. This could be enhanced by the appropriate stirring speed. The feasibility and spontaneity of the adsorption process are confirmed by the negative values of ΔG (−1.6765 to 7.9602 kJ mol⁻¹).

**Desorption mechanism.** Figure 4 shows the comparative effect of different eluents in the desorption of Cu²⁺ from Cu²⁺-loaded nZVI. The opportunity to investigate regeneration and reusability of loaded adsorbent is enhanced by desorption studies. The effectiveness of three different eluents and desorbing agents (HCl, CH₃COOH, and H₂O) was investigated. The basic desorption mechanisms are ion exchange, complexation, and

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**Figure 2.** (A–E): Linearized plots of (A) pseudo-first-order rate equation, (B) pseudo-second-order rate equation, (C) Elovich rate equation, (D) Avrami kinetics models, (E) fractional power rate equation models for adsorption of Cu²⁺ onto nZVI at 10 ppm, 50 ppm, 100 ppm, 150 ppm and 200 ppm.
precipitation depending on the most effective desorbing agent. The exact mechanism involved in the adsorption process is revealed by the performance of the most effective desorbing agent. The maximum percentage of Cu(II) desorbed from Cu(II)-loaded-nZVI using HCl was 79.89% showing the best desorption index of 3.39. The effectiveness of HCl as the best desorbing agent among the three eluents used is supported by the findings of Reddiar et al. (2019). Acetic acid also performed averagely while distilled-deionized water was a poor desorbing agent in the desorption of Cu(II) from Cu(II)-loaded-nZVI. Thus, the adsorption of Cu(II) onto nZVI

| Kinetics model parameters | Initial Cu²⁺ concentration |
|--------------------------|-----------------------------|
|                          | Evaluated parameters        | 10 ppm | 50 ppm | 100 ppm | 150 ppm | 200 ppm |
|                          |                           |        |        |         |         |         |
| PFO                      | qₑ, exp (mg g⁻¹)          | 4.9859 | 24.1981| 43.8152 | 61.684  | 81.77   |
|                          | qₑ, cal (mg g⁻¹)          | 0.01109| 2.1311 | 2.3147  | 3.1261  | 1.5816  |
|                          | kₑ (min⁻¹)                | −0.0164| 8.065×10⁻³| −9.212×10⁻⁴| 4.375×10⁻⁴| 1.152×10⁻²|
|                          | hₑ (mg g⁻¹ min⁻¹)         | 1.785×10⁻⁴| 1.717×10⁻²| 2.22×10⁻³| 1.367×10⁻³| 1.822×10⁻³|
|                          | R²                        | 0.1029 | 0.3549 | 0.0147  | 0.7275  | 0.2127  |

| PSO                      | qₑ, exp (mg g⁻¹)          | 4.9859 | 24.1981| 43.8152 | 61.684  | 81.77   |
|                          | qₑ, cal (mg g⁻¹)          | 5.005  | 24.6305| 42.5532 | 61.728  | 83.333  |
|                          | kₑ (g mg⁻¹ min⁻¹)         | 1.3441 | 0.02813| 3.7301  | 3.8572  | 2       |
|                          | hₑ (mg g⁻¹ min⁻¹)         | 33.67  | 17.0648| 158.73  | 238.095 | 166.667 |
|                          | R²                        | 1      | 0.9999 | 0.9999  | 1       | 0.9999  |

| Elovich                  | qₑ, exp (mg g⁻¹)          | 4.9859 | 24.1981| 43.8152 | 61.684  | 81.77   |
|                          | qₑ, cal (mg g⁻¹)          | 4.9889 | 23.6859| 42.7181 | 61.4962 | 82.3027 |
|                          | a (g min⁻¹ mg⁻¹)          | 6.449×10⁻¹⁵| 1.289×10⁻⁴| −4.39×10⁻²| 1.3162×10⁻⁴| 7.4216×10⁻¹⁵|
|                          | β (g min⁻¹ mg⁻¹)          | 68.9655| 0.755  | −15.0602| 1.7274  | 0.9406  |
|                          | R²                        | 0.9397 | 0.9336 | 0.0078  | 0.9357  | 0.7967  |

| Avrami                   | qₑ, exp (mg g⁻¹)          | 4.9859 | 24.1981| 43.8152 | 61.684  | 81.77   |
|                          | qₑ, cal (mg g⁻¹)          | 4.9906 | 23.6629| 42.7202 | 61.5025 | 82.2843 |
|                          | α (g min⁻² mg⁻¹)          | 6.449×10⁻¹⁴⁵| 1.289×10⁻⁶| −4.39×10⁻²⁸⁵| 1.3162×10⁻⁴⁴| 7.4216×10⁻¹⁴⁵|
|                          | β (g min⁻¹ mg⁻¹)          | 69.9655| 0.755  | −15.0602| 1.7274  | 0.9406  |
|                          | R²                        | 0.9457 | 0.5795 | 0.0065  | 0.9414  | 0.1732  |

| Fractional power         | qₑ, exp (mg g⁻¹)          | 4.9859 | 24.1981| 43.8152 | 61.684  | 81.77   |
|                          | qₑ, cal (mg g⁻¹)          | 4.9906 | 23.6629| 42.7202 | 61.5025 | 82.2843 |
|                          | v (min⁻¹)                 | 2.9×10⁻⁴| 5.83×10⁻²| −1.5×10⁻³| 9.5×10⁻³| 1.3×10⁻²|
|                          | kᵥ (g g⁻¹)                | 4.9295 | 18.638 | 42.9833 | 59.1561 | 78.0189 |
|                          | kᵥv (mg g⁻¹ min⁻¹)        | 1.429×10⁻²| 1.0866 | 6.447×10⁻²| 5.619×10⁻²| 1.0142  |
|                          | R²                        | 0.94   | 0.9311 | 0.0078  | 0.9352  | 0.7967  |

Table 5. Kinetic data for adsorption of Cu²⁺ onto nZVI at different initial concentrations.

Normalized standard deviation Δqₑ (%)  

\[ \Delta qₑ(\%) = 100 \left( \frac{\sum_{i=1}^{n} (qₑ,exp − qₑ,cal)^2}{n-1} \right)^{0.5} \]

Hybrid fractional error function (HYBRID)  

\[ HYBRID = \sum_{i=1}^{n} \left( \frac{qₑ,exp − qₑ,cal}{qₑ,exp} \right) \]

Derivative of Marquardt's percent standard deviation (MPSD)  

\[ MPSD = \sum_{i=1}^{n} \left( \frac{qₑ,exp − qₑ,cal}{qₑ,exp} \right)^2 \]

Average relative error (ARE)  

\[ ARE = \sum_{i=1}^{n} \left( \frac{qₑ,exp − qₑ,cal}{qₑ,exp} \right) \]

Standard deviation of relative errors (Sₑₑₑ)  

\[ Sₑₑₑ = \sqrt{\sum_{i=1}^{n} (qₑ,exp − qₑ,cal)^2 - ARE} \]

Table 6. Adsorption statistical error validity models (ASEVM)²⁴,⁴³,⁴⁴,⁴⁶.

precipitation depending on the most effective desorbing agent. The exact mechanism involved in the adsorption process is revealed by the performance of the most effective desorbing agent. The maximum percentage of Cu(II) desorbed from Cu(II)-loaded-nZVI using HCl was 79.89% showing the best desorption index of 3.39. The effectiveness of HCl as the best desorbing agent among the three eluents used is supported by the findings of Reddiar et al. (2019). Acetic acid also performed averagely while distilled-deionized water was a poor desorbing agent in the desorption of Cu(II) from Cu(II)-loaded-nZVI. Thus, the adsorption of Cu(II) onto nZVI
is routed by ion exchange. Ion-exchange, electrostatic and physiochemical mechanistic nature of the adsorption supported by the previous studies50,58,59.

Conclusion
This study revealed the effectiveness of nZVI as an auspicious nano sorbent for the efficient elimination of endocrine disruptive heavy metal ions. The quality physicochemical properties of nZVI gave it an edge among the list of other nano-adsorbents compared. Evidence of the adsorption of Cu$^{2+}$ onto nZVI was revealed by a change in morphology and elemental distribution by SEM and EDX respectively from post adsorption characterization.

Table 7. Statistical Error validity data on kinetics models of adsorption of Cu(II) onto nZVI.

| Adsorption statistical error validity models on kinetics of adsorption | Data at various initial Cu$^{2+}$ concentrations |
|---|---|
| | 10 ppm | 50 ppm | 100 ppm | 150 ppm | 200 ppm |
| Pseudo first-order | 4.9859 | 24.1981 | 43.8152 | 61.684 | 81.77 |
| $q_e$ (mg g$^{-1}$) | 0.01109 | 2.1311 | 2.3147 | 3.1261 | 1.5816 |
| R$^2$ | 0.1029 | 0.5549 | 0.0147 | 0.7275 | 0.2127 |
| HYBRID | 4.9637 | 20.1236 | 39.3081 | 55.5902 | 78.6374 |
| MPSD | 0.9956 | 0.8316 | 0.8971 | 0.9012 | 0.9617 |
| ARE | 0.9978 | 0.9119 | 0.9472 | 0.9493 | 0.9806 |
| $\Delta q$ | 6.6284 | 6.6284 | 6.6284 | 6.6284 | 6.6284 |
| SRE | 1.98852 | 10.5775 | 20.2777 | 28.8043 | 39.6039 |
| Pseudo second-order | 7.317 × 10$^{-5}$ | 0.00773 | 0.03635 | 3.1 × 10$^{-5}$ | 0.02988 |
| $q_e$ (mg g$^{-1}$) | 5.005 | 24.6305 | 42.5332 | 61.728 | 83.333 |
| R$^2$ | 0.9986 | 0.9833 | 0.9992 | 0.9996 | 0.9989 |
| HYBRID | 1.468 × 10$^{-5}$ | 0.000319 | 0.000883 | 5.09 × 10$^{-7}$ | 0.000365 |
| MPSD | 1.0000001 | -0.00830 | -0.01787 | 0.028803 | -0.00071 |
| ARE | 0.09577 | 0.446729 | 0.72007 | 0.017833 | 0.477865 |
| $\Delta q$ | 0.007634 | 0.2073 | 0.6166 | 0.02164 | 0.7719 |
| Elovich | 4.9859 | 24.1981 | 43.8152 | 61.684 | 81.77 |
| $q_e$ (mg g$^{-1}$) | 4.9889 | 23.6859 | 42.7181 | 61.4962 | 82.3027 |
| R$^2$ | 0.4294 | 0.0791 | 0.8596 | 0.9643 | 0.7837 |
| HYBRID | 1.8051 × 10$^{-6}$ | 0.01084 | 0.02747 | 0.00057 | 0.00347 |
| MPSD | 3.6204 × 10$^{-5}$ | 0.000448 | 0.006027 | 9.27 × 10$^{-4}$ | 0.024 × 10$^{-5}$ |
| ARE | -0.0006017 | 0.021167 | 0.025039 | 0.003045 | -0.00651 |
| $\Delta q$ | 0.015042 | 0.529174 | 0.625981 | 0.076114 | 0.162865 |
| SRE | 0.0011999 | 0.24556 | 0.53603 | 0.09237 | 0.2631 |
| Avrami | 4.9859 | 24.1981 | 43.8152 | 61.684 | 81.77 |
| $q_e$ (mg g$^{-1}$) | 4.873 | 17.5472 | 41.307 | 60.1006 | 78.3886 |
| R$^2$ | 0.4294 | 0.0791 | 0.8596 | 0.9643 | 0.7837 |
| HYBRID | 0.002556 | 1.8280 | 0.1436 | 0.04065 | 0.1398 |
| MPSD | 0.0005127 | 0.07554 | 0.003277 | 0.000659 | 0.00171 |
| ARE | 0.03264 | 0.2748 | 0.05724 | 0.02567 | 0.04135 |
| $\Delta q$ | 0.5861 | 6.8713 | 1.4311 | 0.6417 | 1.0338 |
| SRE | 0.04512 | 3.1880 | 1.2255 | 0.7789 | 1.6700 |
| Power function (fractional power) | 4.9859 | 24.1981 | 43.8152 | 61.684 | 81.77 |
| $q_e$ (mg g$^{-1}$) | 4.9906 | 23.6629 | 42.7202 | 61.5025 | 82.2843 |
| R$^2$ | 0.5443 | 0.5827 | 0.7156 | 0.6609 | 0.6989 |
| HYBRID | 4.43 × 10$^{-5}$ | 0.01184 | 0.02737 | 0.00053 | 0.00323 |
| MPSD | 8.886 × 10$^{-6}$ | 0.000489 | 0.00625 | 8.66 × 10$^{-4}$ | 3.96 × 10$^{-5}$ |
| ARE | -0.000943 | 0.022117 | 0.024991 | 0.002942 | -0.00629 |
| $\Delta q$ | 0.0236 | 0.5529 | 0.6247 | 0.07356 | 0.15724 |
| SRE | 0.001878 | 0.2565 | 0.535004 | 0.089279 | 0.254005 |
Figure 3. Linearized plots of (A) intraparticle diffusion, (B) liquid film diffusivity, (C) external diffusion, (D) Bangham and (E) Boyd models for adsorption of Cu^{2+} onto nZVI at 10 ppm, 50 ppm, 100 ppm, 150 ppm and 200 ppm.

Table 8. Adsorption Mechanism models for Sorption of Cu^{2+} onto nZVI.

| Adsorption mechanism models | Cu^{2+} concentration |
|-----------------------------|-----------------------|
|                             | 10 ppm   | 50 ppm   | 100 ppm  | 150 ppm  | 200 ppm  |
| Intraparticle diffusion     |          |          |          |          |
| \(k_p\) (mg g\(^{-1}\) min\(^{-0.5}\)) | 0.0047   | 0.3993   | -0.0199  | 0.1743   | 0.3224   |
| C                           | 4.9501   | 20.378   | 42.883   | 60.052   | 79.634   |
| \(R^2\)                     | 0.9795   | 0.8321   | 0.0069   | 0.8322   | 0.7185   |
| Liquid film diffusion       |          |          |          |          |
| \(k_{LFD}\)                 | -0.0281  | -0.0259  | -0.0009  | 0.0043   | -0.0211  |
| C                           | -6.5233  | -2.6199  | -2.9337  | -3.0157  | -5.0927  |
| \(R^2\)                     | 0.1855   | 0.6484   | 0.0147   | 0.7275   | 1.552    |
| External diffusion          |          |          |          |          |
| \(k_{ext}\)                 | -0.0281  | 0.0143   | 0.0003   | 0.0008   | 0.0012   |
| C                           | -6.5233  | -2.0416  | -0.0119  | -1.6533  | -1.6452  |
| \(R^2\)                     | 0.1855   | 0.7597   | 0.0119   | 0.7058   | 0.6417   |
| Bangham                     |          |          |          |          |
| \(\alpha\)                  | 0.003    | -0.0047  | 0.0004   | 0.00008  | 0.0133   |
| \(K_0\)                     | 0.025285 | 1.8564   | 2.1820   | 2.4858   | 0.019896 |
| \(R^2\)                     | 0.9404   | 0.9344   | 0.0078   | 0.9351   | 0.7968   |
| Boyd                        |          |          |          |          |
| \(R^2\)                     | 0.1623   | 0.6170   | 0.0147   | 0.7275   | 0.1258   |
The adsorption of Cu\textsuperscript{2+} onto nZVI was well influenced by operational parameters. Optimum adsorption was achieved at pH 6 with 98.31% removal efficiency, 73.73 mg g\textsuperscript{-1} quantity adsorbed and 200 rpm stirring speed. Thermodynamics parameters \(\Delta H^\circ (\pm 50.6059 \text{ kJ mol}^{-1})\), \(\Delta S^\circ (174.6790 \text{ J mol}^{-1} \text{ K}^{-1})\), \(\Delta G^\circ (\pm 1.6765 \text{ kJ mol}^{-1} \text{ to } -7.9602 \text{ kJ mol}^{-1})\). Indicated random, feasible, spontaneous, and endothermic nature of the adsorption process. The adsorption behavior was well explained by the Langmuir isotherm model and it followed the following order: Langmuir > Jossen/Elovich > Freundlich/Halsey > Temkin > Fowler–Guggenheim > Redlich–Peterson > DKR > Flory–Huggins > Kiselev > Harkin–Jura > Jovanovic. Langmuir best described equilibrium data. The Langmuir monolayer adsorption capacity (90.09 mg g\textsuperscript{-1}) surpassed other nano-adsorbents utilized for the adsorption of Cu(II) ion. The Pseudo-second-order (PSO) best described the kinetics model based on \(R^2\) values greater than 0.99, close agreement between \(q_e, \text{exp}\) and \(q_e, \text{cal}\) and lower values of the five rigorous statistical validity models (\(\Delta q_t, \text{ARE, HYBRD, MPSD, and SRE}\)). The mechanism model was pore diffusion dependent. Best desorption capacity and the index was portrayed by HCl indicating that ion-exchange, electrostatic, and physisorption mechanism. Based on the capacity displayed by nZVI in adsorption of EDC Cu\textsuperscript{2+}, it could be recommended for effective industrial treatment of heavy metal ions.

**Data availability**

Available data are presented in the study and no other data were used to support the study.

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Table 9. Thermodynamic parameters for adsorption of Cu\textsuperscript{2+} onto nZVI.

| T(K) | \(\Delta G (\text{kJ mol}^{-1})\) | \(\Delta H (\text{kJ mol}^{-1})\) | \(\Delta S (\text{J mol}^{-1} \text{ K}^{-1})\) | Kc  |
|------|----------------------|----------------------|----------------------|-----|
| 298  | − 1.6765             | + 50.6059            | 174.679             | 1.9671 |
| 308  | − 2.8163             |                      |                     | 3.00304 |
| 318  | − 4.4575             |                      |                     | 5.39623 |
| 328  | − 7.7182             |                      |                     | 16.9419 |
| 338  | − 7.9602             |                      |                     | 16.9825 |

**Figure 4.** Comparative effect of different eluents in the desorption of Cu\textsuperscript{2+} from Cu\textsuperscript{2+}-loaded nZVI.
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Author contributions
A.O.D., F.A.A., E.O.O., A.S.O. carried out the experiments, analyzed the results for the adsorption data. A.O.D., F.A.A., E.O.O., O.S.B. fitted the thermodynamics and kinetics of adsorption curves. A.O.D., F.A.A., and E.O.O., A.S.O. carried out the experiments, analyzed the results for the adsorption data. A.O.D., F.A.A., E.O.O., A.S.O. carried out the experiments, analyzed the results for the adsorption data. A.O.D., F.A.A., E.O.O., O.S.B. drafted the manuscript. All authors reviewed and approved the manuscript.

Competing interests
The authors declare no competing interests.

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Correspondence and requests for materials should be addressed to A.O.D.

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