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Adsorption of copper ions onto nano-scale zero-valent iron impregnated cashew nut shell

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ABSTRACT

In this work, the synthesis and characterization of a new low-cost adsorbent such as nano-scale zero-valent iron impregnated cashew nut shell (NZVI-CNS) was studied for the removal of copper ions. The prepared adsorbent was characterized by Fourier Transform Infrared Spectroscop, Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy, Transmission Electron Microscopy, and X-ray diffraction. The adsorption parameters such as solution pH, adsorbent dose, initial copper ions concentration, contact time, and temperature were optimized. The adsorption kinetics of copper ions removal by NZVI-CNS have been studied by pseudo-first-order, pseudo-second-order, intraparticle diffusion, Boyd kinetic, and shrinking core models. The adsorption isotherms of copper ions removal by NZVI-CNS have been studied by Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich models. The adsorption experimental data were best fitted with the pseudo-second-order and Freundlich models. The thermodynamic studies showed the adsorption process was spontaneous, feasible, and exothermic in nature. The results indicated that NZVI-CNS can act as an effective adsorbent for the removal of heavy metal ions from the water/wastewater by reducing its intake in the human food chain.

Keywords: Adsorption; Copper ions; Isotherm; Kinetics; NZVI-CNS

1. Introduction

The presence of heavy metal ions in the aquatic system causes serious health hazards to the human beings and also other living organisms [1–3]. Copper ions are one of the toxic heavy metal ions which were discharged from the different industries such as metal cleaning and plating baths, paints and pigments, mining and smelting, brass manufacturing, petroleum refining, fertilizer, paper board, wood pulp, and printed circuit board production [4–6]. The wastewater from these industries frequently contain considerable amount of copper ions, which spread into the environment through soil and aquatic streams and finally gets accumulated along the food chain causing health

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hazards to the human beings. Copper is an important metal for living organism at lower concentration, but it produces severe toxic effects at higher concentrations. Generally, the copper do not degrade in the environment, but its existence in the earth surface reduces the activity of the living organisms. The excessive intake of copper ions by the human beings leads to the severe mucosal irritation and corrosion, hepatic and renal damage, widespread capillary damage, kidney damage and anemia, and irritation of the central nervous system followed by depression. According to the Bureau of Indian Standards, the permissible limit of copper ions in drinking water is 0.05 mg/L [7].

A variety of treatment technologies have been applied for the removal of heavy metal ions including chemical precipitation, ion exchange, adsorption, solvent extraction, membrane filtration, coagulation–flocculation, flotation, and electrochemical technologies [3,8,9]. Most of the technologies are expansive and unable to remove the trace levels of heavy metal ions from the aqueous solution. Among these separation technologies, adsorption process offers flexibility and simple in design, convenience and ease of operation, and effective in the removal of heavy metal ions especially at lower metal ions concentration [9]. Many adsorbents such as activated carbons, zeolites, clays, biomass, polymeric materials, and other adsorbents have been widely used for the removal of heavy metal ions from the wastewaters [5,10–12]. But, many adsorbents have low adsorption capacities, poor regeneration abilities, and separation problems. Therefore, still the research is being available in the process for the generation of new low-cost adsorbents particularly for the removal of heavy metal ions from the water/wastewater. An excellent adsorbent should have a higher adsorption capacities, better regeneration abilities, and shorter equilibrium time for the maximum removal of metal ions. For the above said reasons, the low-cost adsorbent materials were synthesized and it was successfully applied for the removal of heavy metal ions from the aqueous solution. A number of low-cost adsorbent materials have been studied for the removal of toxic heavy metal ions, including coconut shell [5], neem leaves [5], hyacinth roots [5], rice straw [5], rice bran [5], rice husk [5], wheat straw [13], soya bean straw [13], corn [13], corn cob [13], and pecan nut shell [14]. These adsorbents were successful for the removal of heavy metal ions at different scales, but the problems are still associated with the excising natural/agricultural wastes as an adsorbent and which are not able to satisfy the actual adsorbent properties.

Nano-scale zero-valent iron (NZVI) is an emerging technology, which is being successfully used for the removal of different metallic ions from its aqueous solutions [15]. Recently, many adsorption experimental studies have been studied for the removal of heavy metal ions from the aqueous solution using nano-scale iron particles [15–20]. The different methods were available for the preparation of zero-valent iron (ZVI) such as sonochemical, chemical vapor condensation, thermal decomposition, and chemical reduction. The main problem for using the ZVI is its accumulation in the effluent after the treatment. To overcome this problem, in this study, an attempt has been made to prepare the NZVI impregnated cashew nut shell (CNS) with the help of the sonication operation for better impregnation. The prepared nano-scale zero-valent iron impregnated cashew nut shell (NZVI-CNS) was utilized as an effective adsorbent for the removal of copper ions from the aqueous solution. The adsorbent was characterized by Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy, Transmission Electron Microscopy (TEM), and X-ray diffraction (XRD) analyses. The adsorption properties for copper ions removal were investigated by batch adsorption experiments, and the experimental data were fitted by the thermodynamic, isotherm, design, kinetic, and mechanism models.

2. Experimental

2.1. Preparation of NZVI-CNS

The preparation of adsorbent, that is NZVI impregnated with support material, that is CNS, was carried out by simple liquid-phase reduction process [21]. About 1.0 g of CNS powder was first washed with water and then soaked in saturated $FeSO_4{\cdot}7H_2O$ solution (6.5 g in 25 mL with 2 drops of concentrated H_2SO_4) for half an hour. After that, the soaked CNS along with the saturated $FeSO_4{\cdot}7H_2O$ solution was sonicated in an ultrasonic bath (SONICS Vibra Cell, 750 Watts) for another half an hour. During sonication, the CNS particle gets broken down into small pieces. After sonication, 0.1 mol/L $NaBH_4$ was added slowly at ambient temperature, pressure, and atmosphere. The ferrous ion impregnated into the CNS was reduced to ZVI as per the following reaction [22,23]:

$$\begin{aligned}&2\text{Fe}^{2+}_{(\text{aq})} + \text{BH}^{-}_{4\,(\text{aq})} + 2\text{H}_2\text{O} + \text{support}\\&\rightarrow 2\text{Fe}^{0}/\text{support}_{(\text{s})} + \text{BO}^{-}_{2\,(\text{aq})} + 4\text{H}^{+}_{(\text{aq})} + 2\text{H}_2\ (\text{g})\end{aligned} \tag{1}$$

The evolution of hydrogen gas was ceased, and the water was decanted. The CNS system was washed with double-distilled water followed by a wash with methanol to prevent the rust formation. The CNS system was dried and stored in an oxygen-free nitrogen environment. The prepared material was termed as

NZVI impregnated CNS (NZVI-CNS). The prepared adsorbent was characterized by FT-IR, FE-SEM EDAX, TEM, and XRD analyses. The particles of boron were formed during the synthesis of ZVI. The separate and special care must be taken for the boron particles because these particles are toxic in nature [21].

2.2. Preparation of copper ions solution

All the chemicals used were of analytical reagents grade. A stock solution of 100 mg/L of copper ions was prepared by dissolving the measured amount of $CuSO_4{\cdot}5H_2O$ (Merck, India) in double-distilled water. Using appropriate subsequent dilution of stock solution, the desired test solutions of copper ions were prepared (20–100 mg/L). Before mixing the adsorbent with the aqueous solution, the pH of each test solution was adjusted to the required value with 0.1 M NaOH or 0.1 M HCl. The concentration of copper ions in the solutions was determined by SL176 Atomic absorption spectrophotometer (AAS, Elico Model, India). The pH of solution was measured using pH meter (Elico Model, India).

2.3. Adsorption experiments

Batch adsorption experiments were conducted to optimize the process parameters such as solution pH, adsorbent dose, contact time, initial copper ions concentration, and temperature on the maximum removal of copper ions from the aqueous solution using NZVI-CNS. For the batch adsorption experimental studies, 100 mL of copper ions solution with different initial copper ions concentrations (20–100 mg/L), pH (2.0–8.0), amount of the adsorbent (0.5–3.0 g/L) and at specified temperature (30–60°C) was taken in a 100 mL conical flasks and then mixture was agitated in an incubation shaker. The samples were withdrawn at different time intervals (0–60 min), and the samples were analyzed for copper ions concentration measurement. Adsorption isotherms, kinetics, mechanism, and thermodynamics were performed systematically. After adsorption experiments, the spent adsorbent was separated using centrifugation and the supernatant was analyzed using (AAS, SL176 Model, Elico Limited, Chennai, India). The percentage of copper ions removal was estimated using the following equation:

$$\%\ \text{Removal} = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \tag{2}$$

where C_o (mg/L) and C_e (mg/L) are the initial and equilibrium concentration of copper ions solution, respectively.

2.3.1. Adsorption thermodynamic experiments

The thermodynamic study was carried out by adding 0.2 g of NZVI-CNS in a series of conical flasks which consists of 100 mL of copper ions solution with the various initial copper ions concentrations ranging from 20 to 100 mg/L. The adsorption systems were kept in an incubation shaker, which was operated under different temperature conditions ranging from 303 to 333 K at an optimum condition. Once the system reached the equilibrium time, the spent NZVI-CNS was separated from the supernatant by means of centrifugation operation. The residual concentration of copper ions in the supernatant was measured with the help of AAS. The values of the thermodynamic parameters such as change in free energy (ΔG°), change in enthalpy (ΔH°), and change in entropy (ΔS°) were estimated from the following equations:

$$K_c = \frac{C_{Ae}}{C_e} \tag{3}$$

$$\Delta G^o = -RT \ln K_c \tag{4}$$

$$\log\left(\frac{C_{Ae}}{C_e}\right) = \frac{\Delta S^o}{2.303\ R} - \frac{\Delta H^o}{2.303\ RT} \tag{5}$$

where K_c is the equilibrium constant, C_{Ae} is the amount of copper ions loaded onto the NZVI-CNS per liter of solution at equilibrium (mg/L), C_e is the concentration of copper ions in the solution at equilibrium (mg/L), R is the gas constant (8.314 J/mol/K), and T is the temperature (K).

2.3.2. Adsorption isotherm experiments

Adsorption isotherm experiments were performed by adding 0.2 g of dried NZVI-CNS samples into 100 mL of the copper ions solution with the various initial copper ions concentrations in the range of 20–100 mg/L at an optimum condition, and then, the mixtures were shaken in an incubation shaker until its equilibrium time. Finally, the spent NZVI-CNS was separated from the mixtures by centrifugation operation, and the concentration of copper ions in the supernatant was analyzed by AAS. The two-parameter adsorption isotherm models such as Langmuir [24], Freundlich [25], Temkin [26], and Dubinin–Radushkevich [27] models were used to explain the copper ions adsorption from aqueous solution. The applicability of these models was compared by the coefficient of correlation (R^2) values and error values (sum of squared error (SSE) and root mean squared error (RMSE)). These two-parameter adsorption isotherm models are as follows:

Langmuir isotherm model:

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

and the equilibrium parameter is:

$$R_L = \frac{1}{1 + K_L C_o} \tag{7}$$

Freundlich isotherm model:

$$q_e = K_F \, C_e^{1/n} \tag{8}$$

Temkin isotherm model:

$$q_e = B \, \ln \, (A \, C_e) \tag{9}$$

Dubinin–Radushkevich isotherm model:

$$q_e = q_{m,D} \, \exp \left(-\beta \, (RT \, \ln \, (1 + 1/C_e))^2 \right) \tag{10}$$

and the mean free energy, E is:

$$E = \frac{1}{\sqrt{2\beta}} \tag{11}$$

where q_e is the equilibrium adsorption amount of copper ions adsorbed on NZVI-CNS (mg/g), q_m is the maximum monolayer adsorption amount of copper ions adsorbed onto NZVI-CNS (mg/g), K_L is the Langmuir constant related to the affinity of the copper ions to the adsorbent (L/mg), C_e is the equilibrium concentration of copper ions solution (mg/L), K_F is the constant ((mg/g)(L/mg)$^{(1/n)}$) related to the adsorption capacity of the adsorbent, n is the constant related to the intensity of the adsorption (g/L), $B = RT/b$, is the constant related to the heat of adsorption, b is the heat of adsorption (kJ/mol), R is the gas constant (8.314 J/mol K), T is the temperature (K), A is the equilibrium binding constant related to the maximum binding energy (L/mg), $q_{m,D}$ is the Dubinin–Radushkevich monolayer adsorption capacity (mg/g), and β is a constant related to adsorption energy.

2.3.4. *Adsorption kinetics and mechanism experiments*

The copper ions removal using NZVI-CNS was done by mixing 0.2 g of NZVI-CNS in 100 mL of copper ions solution (20–100 mg/L) in series of conical flasks. The conical flasks were kept in an incubation shaker, and the samples were withdrawn at specified time intervals (10–60 min). After centrifugation operation, the residual concentration of copper ions in the supernatant was analyzed by AAS. The amount of copper ions adsorbed onto NZVI-CNS at time t, q_t (mg/g), was calculated by the following expression:

$$q_t = \frac{(C_o - C_t) \, V}{m} \tag{12}$$

where C_t is the concentration of copper ions in the solution at time t (mg/L), V is the volume of copper ions solution (L), and m is the mass of the NZVI-CNS (g). The adsorption kinetic data were used to test the adsorption kinetic models such as pseudo-first-order [28] and pseudo-second-order [29] kinetic models to explain the adsorption process. The adsorption kinetic models are given as follows:

Pseudo-first-order kinetic model:

$$\log \, (q_e - q_t) = \log \, q_e - \frac{k_1}{2.303} \, t \tag{13}$$

Pseudo-second-order kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{14}$$

where q_e is the equilibrium adsorption capacity (mg/g), q_t is the adsorption capacity at any time t (mg/g), k_1 is the pseudo-first-order kinetic rate constant (min^{-1}), t is the time (min), k_2 is the pseudo-second-order kinetic rate constant (g/mg min), and $k_2 \cdot q_e{}^2 = h$, is the initial adsorption rate (mg/g min).

The adsorption mechanism was described by fitting the adsorption kinetic data to the different adsorption mechanism models such as intraparticle diffusion [30], Boyd kinetic [31], and shrinking core models [32–34]. The adsorption mechanism models were given as follows:

Weber and Morris intraparticle diffusion model:

$$q_t = k_p t^{1/2} + C \tag{15}$$

The Boyd kinetic model:

$$-0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right) = Bt \tag{16}$$

The effective diffusivity D_i (m^2/s) values were estimated using the following equation:

$$B = \frac{\pi^2 D_i}{r^2} \tag{17}$$

where q_t is the adsorption capacity at any time t (mg/g), k_p is the intraparticle diffusion constant (mg/g $\text{min}^{0.5}$), t is the time (min), C is a constant related to the thickness of the boundary layer, and r is the radius of the SMSP. The shrinking core model (SCM) was successfully used to fluid-particle chemical reactions by Levenspiel [32].

For film diffusion control:

$$X = \frac{3D}{\delta\, r\, C}\alpha \tag{18}$$

If the film diffusion is controlled in the removals of copper ions by NZVI-CNS, then the plot of X vs. α yields a straight line.

For particle diffusion control:

$$\mathrm{F}(X) = 1 - 3(1 - X)^{\frac{2}{3}} + 2(1 - X) = \frac{6D}{r^2 C^{\mathrm{o}}}\alpha \tag{19}$$

If the particle diffusion is controlled in the removals of copper ions by NZVI-CNS, then the plot of F(X) vs. α give a straight line. The diffusivity values can be calculated from the slope of the plots.

$$D = (\text{Slope})\frac{C^{\mathrm{o}} r^2}{6} \tag{20}$$

where

$$X \text{ is the extent of reaction} = \frac{(C_{\mathrm{o}} - C)}{(C_{\mathrm{o}} - C_{\mathrm{eq}})} \tag{21}$$

$$\alpha = \int_0^t C\, \mathrm{d}t \tag{22}$$

where C_{o} is the initial copper ions concentration (mg/L), C^{o} is the average copper ions binding site density of the NZVI-CNS (mg/L), C is the final copper ions concentration (mg/L), C_{eq} is the equilibrium concentration of copper ions (mg/L), D is the diffusion coefficient (m^2/s), and r is the radius of the NZVI-CNS particles (m).

3. Results and discussion

3.1. Characterization of the adsorbent

The chemical functional groups such as carbonyl, hydroxyl, amide, metal oxide, and iron oxide have been identified as a potential adsorption sites which are responsible for the binding of metallic ions to the adsorbent. The adsorption capacity of NZVI-CNS depends upon the porosity as well as chemical reactivity of functional groups at the surface. This reactivity creates an imbalance between the forces at the surface when compared to those within the body, thus leading to molecular adsorption by the van der Waals force. Knowledge on the surface functional groups would give an insight of the adsorption capability of the NZVI-CNS. The FT-IR spectrum of the NZVI-CNS is shown in Fig. 1. The strong peak at 3,372 and 1,657 cm^{-1} corresponds to O–H stretching vibrations. The strongest peak in the region of 2,850–3,000 cm^{-1} corresponds to alkane C–H stretching mode. The peak in the region 2,100–2,260 cm^{-1} resembles the C=C alkyne stretching mode. The continuous two bands at 1,300–1,385 cm^{-1} refers to N–O stretching mode. The presence of strongest peak at the region of 1,109 cm^{-1} corresponds to the stretching mode of C–O alcohol. The peak at the region of 600–400 cm^{-1} refers to the metal oxide which indicates the presence of iron oxide in the adsorbent. The FT-IR studies revealed that the several functional groups were available on the adsorbent surface, which are able to remove the copper ions from the aqueous solution.

The size and shape of the adsorbent impact the adsorption capacity of the adsorbent. The FE-SEM image of the NZVI-CNS is shown in Fig. 2. The surface of the adsorbent appears to be irregular and porous ranging in size from 20 to 200 nm that forms aggregates and chains, due to magnetic attractive forces between the particles. This small NZVI-CNS particle size provides a larger surface area for contaminant adsorption. On the basis of this fact, it can be concluded that the adsorbent has an adequate morphology for copper ions adsorption. Fig. 2 shows the high-resolution EDX spectrum of NZVI-CNS and its chemical composition. The rod shape-like particles are iron, whereas the matrix is CNS. The surface looks uniform because the micro-holes formed during the sonication which has been filled with NZVI. The presence of iron and carbon in the chemical composition confirms the impregnation of NZVI into the CNS. The percentage of iron was found to be of 8.71% and the carbon was

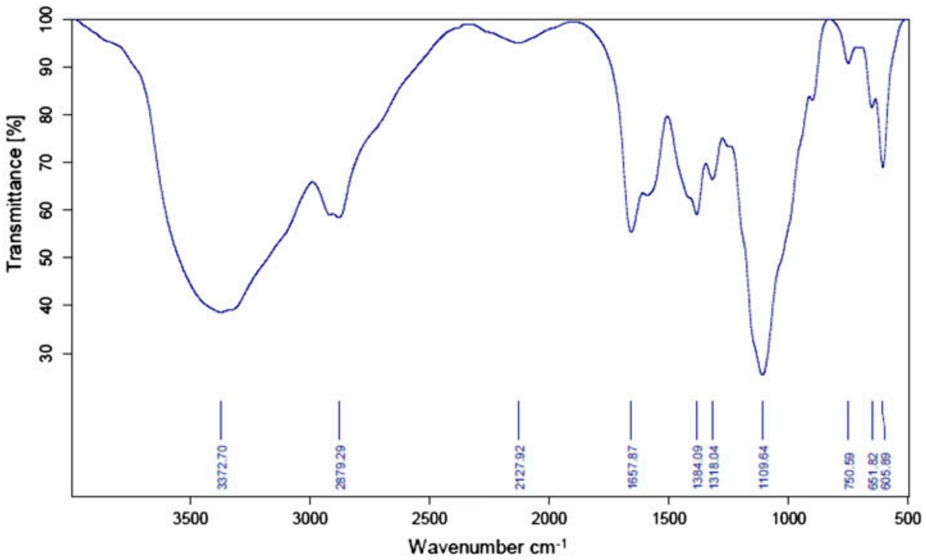

Fig. 1. FT-IR spectrum of NZVI-CNS.

found to be of 40.81%. The energy spectrum indicates that the only reducing agent present in the CNS is iron. The TEM analysis was used to investigate the morphology and size distribution of NZVI-CNS (Fig. 3). It was found that the sample NZVI-CNS formed a chain-like aggregated structure because of its natural tendency to remain in a more thermodynamically stable state. Fig. 3 showed that NZVI-CNS has very thin layers of iron oxide shells with distinguishable dark portions inside because of Fe^o.

XRD was used to investigate the crystallinity of NZVI-CNS. The chemical composition and crystallinity of the sample NZVI-CNS are presented in Fig. 4. Here, it was observed that the diffractograms are same and in good agreement with the XRD pattern of NZVI. But some undesired peaks have been observed due to the impurity phase present in the sample. The XRD has shown the powder XRD pattern of NZVI samples under ambient conditions. The broad peak revealed the existence of an amorphous phase of iron. The characteristic broad peak at 2θ of 45° indicated that the zero-valent iron was predominantly present in the sample. The pattern was indexed with hexagonal cell structure consistent with JCPDS card 36-13 51. From the XRD pattern, the particle size of the NZVI nano particle was found to be 40–56 nm. This indicated that the sample synthesized by sonication has higher crystallinity than other conventional methods.

3.2. *Effect of different operating parameters*

The pH of the copper ions solution is one of the most important factors for the adsorption of copper ions onto NZVI-CNS. The effect of solution pH on the adsorption process is shown in Fig. 5. The adsorption experiments were carried out in the initial pH range of 2.0–8.0. At low pH, the removal and equilibrium adsorption capacity (q_e) values are low as the number of available hydronium ions is high in the solution and the copper ions compete with them for the adsorption sites. Point of zero charge (pH_{pzc}) is the pH at which the adsorbent surface is neutral. At $pH > pH_{pzc}$, the negative charges on the adsorbent surfaces was increased; hence, the cation adsorption capacity gets increased. In the present adsorption system, pH_{pzc} of the adsorbent was found to be greater than 6.0 and it was indicated that at $pH > 6$, copper ions precipitated as copper hydroxide. So, the pH 6.0 was considered to be an optimum pH for the present adsorption system.

The effect of adsorbent dosage on the adsorption of copper ions by the NZVI-CNS is shown in Fig. 6. From Fig. 6, it was observed that the removal of copper ions were increased with the increase in dosage of NZVI-CNS, but the equilibrium adsorption capacity (q_e) was decreased. This may be due to the increase in number of available active sites with the increase in the NZVI-CNS dosage. The results show that 2.0 g/L has enough exchangeable sites for the removal of copper ions. It was also observed that the removal of copper ions was not changed after 2.0 g/L of NZVI-CNS. This indicated that after a certain dosage of NZVI-CNS, the maximum removal of copper ions was observed, and hence, the amount of copper ions adsorbed onto the NZVI-CNS and the amount of free copper ions remain constant even with further addi-

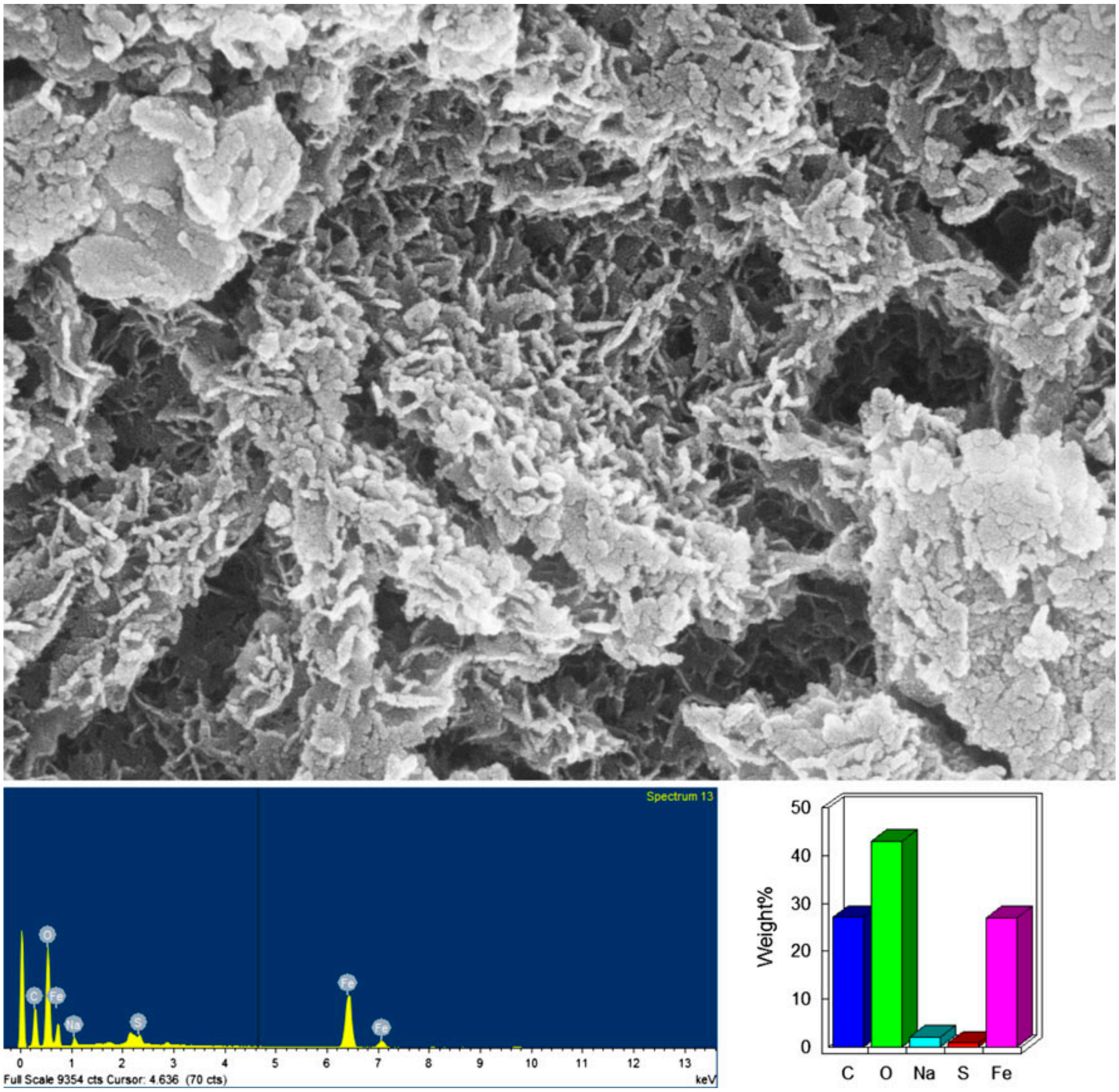

Fig. 2. SEM EDX analysis of NZVI-CNS.

tion of the dosage of NZVI-CNS. The optimum dosage of NZVI-CNS was found to be of 2 g/L for the present adsorption system.

As shown in Fig. 7, the equilibrium adsorption capacity (q_e) was increased with increase in the initial copper ions concentration; however, the percentage removal of copper ions was decreased. The q_e values were increased from 9.9983 to 45.039 mg/g; while the percentage removal was decreased from 99.983 to 90.078% for an initial copper ions concentration from 20 to 100 mg/L, respectively. At higher initial copper ion concentration, the number of moles of copper ions available to the surface area was high, so the functional adsorption depends on the initial copper ions concentration. This adsorption behavior observed that the surface saturation depends on the initial copper ions concentration. This initial copper ions concentration provides the driving force to overcome all mass transfer resistance of copper ions between the aqueous solution and solid adsorbent. At lower copper ions concentration, the ratio of surface active sites to the copper ions in the aqueous solution might be high, and hence, all the copper ions may interact with the solid adsorbent and the copper ions was removed from the aqueous solution.

The batch adsorption studies were carried out in different time intervals, and the results are shown in

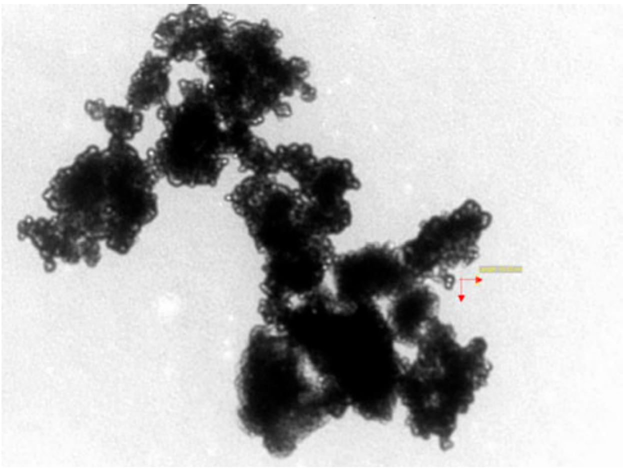

Fig. 3. TEM image of NZVI-CNS.

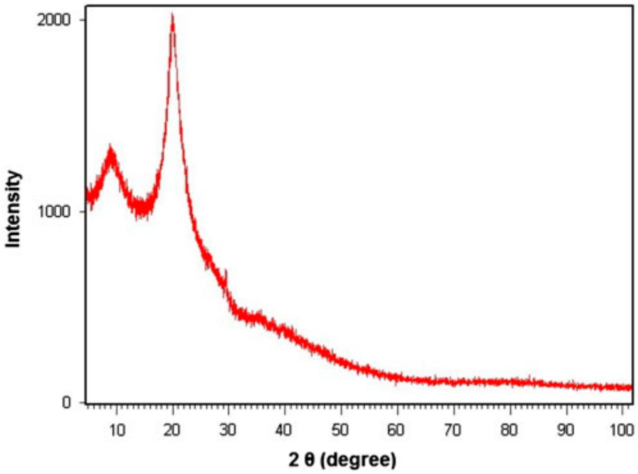

Fig. 4. XRD image of NZVI-CNS.

Fig. 8. From Fig. 8, it was observed that the removal of copper ions and equilibrium adsorption capacity was initially quite high, followed by a much slower subsequent removal rate which leads to the gradual reach of an equilibrium condition approximately after 30 min. Further increase in contact time did not showed any increase in adsorption. At initially, the percentage removal and q_e values were higher which may be due to a larger surface area of the adsorbent being available for the removal of copper ions. Less removal in the later stage may be due to the problem faced by the copper ions to occupy the remaining vacant sites in the adsorbent because of the forces between the copper ions in the solid and aqueous

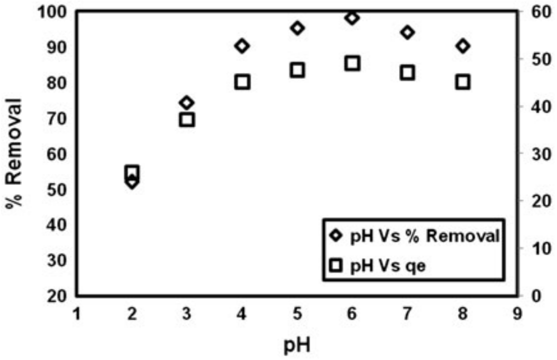

Fig. 5. Effect of solution pH for the adsorption of copper ions by NZVI-CNS (copper ions concentration = 40 mg/L, adsorbent dose = 2 g/L, volume of sample = 100 mL, equilibrium time = 30 min, and temperature 30˚C).

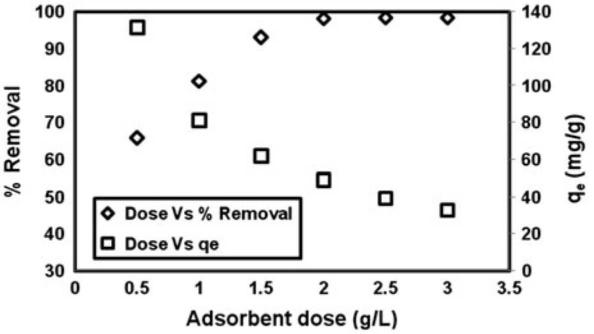

Fig. 6. Effect of adsorbent dose for the adsorption of copper ions by NZVI-CNS (copper ions concentration = 40 mg/L, solution pH = 5.0, volume of sample = 100 mL, equilibrium time = 30 min, and temperature 30˚C).

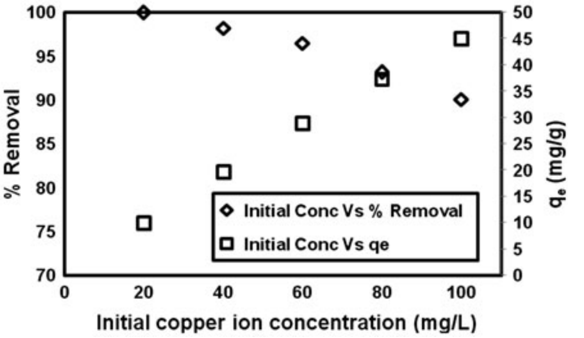

Fig. 7. Effect of initial copper ions concentration for the adsorption of copper ions by NZVI-CNS (copper ions concentration = 20–100 mg/L, solution pH = 5.0, adsorbent dose = 2 g/L, volume of sample = 100 mL, equilibrium time = 30 min, and temperature 30˚C).

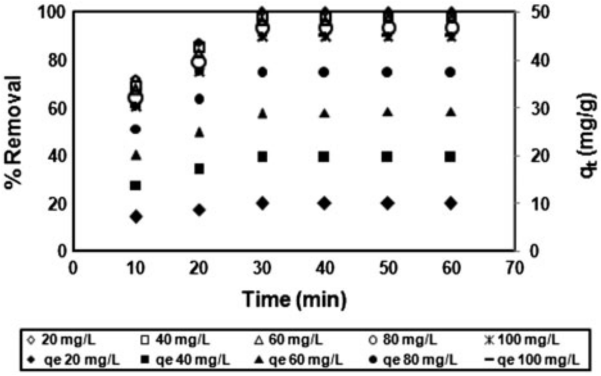

Fig. 8. Effect of contact time for the adsorption of copper ions by NZVI-CNS (copper ions concentration = 20–100 mg/L, solution pH = 5.0, adsorbent dose = 2 g/L, volume of sample = 100 mL, and temperature 30˚C).

phase. The less removal with the increasing time may also be due to that the intraparticle diffusion process may dominate the adsorption process at later stages of adsorption. From Fig. 8, it was observed that the two stage of adsorption mechanism, that is first, rapid and quantitatively predominant and the second, slower and quantitatively insignificant. The results indicated that the NZVI-CNS can be used as an effective adsorbent for the fast removal of copper ions from the water/wastewater.

The influence of temperature on the removal of copper ions by NZVI-CNS was investigated for different temperatures ranging from 30 to 60˚C at an optimum condition, and the results are depicted in Fig. 9. It can be seen that the percentage removal was decreased with the increase in the temperature from 303 to 333 K. This indicates the adsorption of copper ions on NZVI-CNS was exothermic in nature. The decrease in the rate of removal of copper ions with the increase in the temperature may be attributed to the weakening of adsorptive forces between the active sites of the adsorbent and copper ions and also between the adjacent copper ions of the adsorbed copper ions in the adsorbent surface. The maximum adsorption was observed at 30˚C for the present adsorption system.

3.3. Evaluation of thermodynamic parameters

The thermodynamic parameters give comprehensive information on inherent energetic changes which are associated with the adsorption process. Therefore, the thermodynamic parameters such as change in free energy (ΔG°), change in enthalpy (ΔH°), and change in entropy (ΔS°) were used to explain the thermodynamic behavior of the adsorption of copper ions onto NZVI-CNS. The plot of log K_c vs. $1/T$ (Fig. 10) gave a straight line, and the values of ΔH° and ΔS° were calculated from the slope and intercept, respectively. The values of estimated thermodynamic parameters are given in Table 1. From Table 1, it can be seen that the negative value of ΔG° at different temperatures confirmed the feasibility of the adsorption process and spontaneous nature. Moreover, the increase in the negative value of ΔG° with the decrease in the temperature indicates that the adsorption process becomes more favorable at lower temperatures. This is possible because the increase of temperature enhanced the movement of copper ions previously adsorbed, which generated a trend of desorbing copper ions from the NZVI-CNS surface. The magnitude of ΔG° may also explain the type of adsorption process. The significance of ΔG° is given as follows: for physical adsorption: −20 to 0 kJ/mol; chemical adsorption: −80 to −400 kJ/mol [35]. So, it was found that the present adsorption system was a physical process. The values

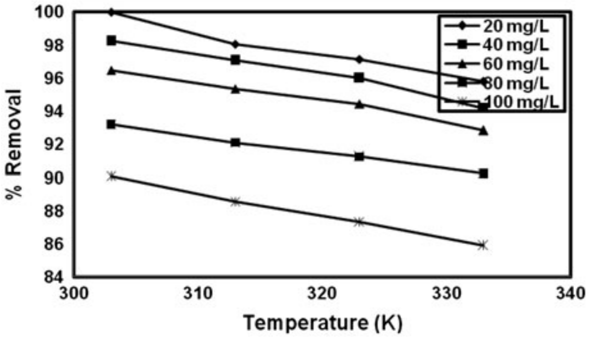

Fig. 9. Effect of temperature for the adsorption of copper ions by NZVI-CNS (copper ions concentration = 20–100 mg/L, solution pH = 5.0, adsorbent dose = 2 g/L, volume of sample = 100 mL, equilibrium time = 30 min, and temperature 30˚C).

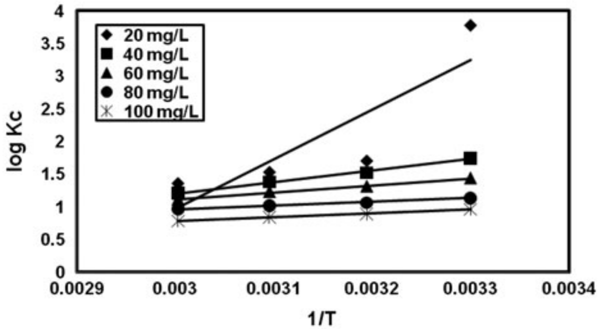

Fig. 10. Thermodynamic analysis for the adsorption of copper ions by NZVI-CNS.

Table 1
Thermodynamic parameters for the adsorption of copper ions onto the NZVI-CNS

Initial conc. of copper ions solution (mg/L)	ΔH° (kJ/mol)	ΔS° (J/mol/K)	ΔG° (kJ/mol) 30℃	40℃	50℃	60℃
20	−145.403	−417.79	−21.865	−10.188	−9.445	−8.650
40	−33.795	−78.427	−10.107	−9.091	−8.520	−7.692
60	−20.507	−40.228	−8.339	−7.857	−7.592	−7.086
80	−10.847	−14.111	−6.594	−6.388	−6.293	−6.158
100	−11.044	−18.155	−5.557	−5.323	−5.189	−4.998

of ΔH^o were found to be negative, indicating that the adsorption process was exothermic in nature which may be due to the weak interaction between the copper ions and NZVI-CNS. From the Table 1, it was also found that the negative values of ΔS° indicates the randomness at the solid–liquid interface in the adsorption system decreases during the adsorption process. For all cases, the decrease in ΔS° might be attributed to the fact that the adsorbate molecules lose at least one degree of freedom when it gets adsorbed onto the adsorbent [36]. The values of ΔH° were found to be greater than $T\Delta S^\circ$ for all initial copper ions concentrations at all temperatures. This points out that the adsorption processes were over-influenced by the enthalpy rather than entropy changes [37].

3.4. Evaluation of adsorption isotherm parameters

Adsorption isotherm gives the relationship between the adsorbate on the adsorbent and adsorbate in the liquid solution at an equilibrium condition. This is a fundamental importance in optimizing the design of an adsorption system for the adsorption of adsorbates and the analysis of adsorption isotherm data by fitting them to different adsorption isotherm models which can be used for the design of adsorption system. In this study, the Langmuir [24], Freundlich [25], Temkin [26], and Dubinin–Radushkevich [27] models were used to calculate the adsorption equilibrium between the copper ions and NZVI-CNS. The validity of these adsorption isotherm models were checked by applying the adsorption equilibrium data (C_e vs. q_e) to these adsorption isotherm models using MATLAB R2009a, and the results are depicted in Fig. 11. The calculated values of adsorption isotherm parameters (q_m, K_L, K_F, n, B, A, $q_{m,D}$, and β) along with the coefficient of determination (R^2) values and error values (SSE and RMSE) are summarized in Table 2. Based on the R^2 and error values from Table 2, the adsorption equilibrium data can be well described by the Freundlich adsorption isotherm model. Also, the Freundlich model yields a best fit to the experimental data than the Langmuir, Temkin, and Dubinin–Radushkevich models. In principle, the Freundlich adsorption isotherm is an empirical model for adsorbent with very uneven adsorbing surface, and this was applicable for the adsorption of single adsorbates within a fixed range of concentration. The value of n gives an idea about the degree of non-linearity between the solution concentration, and adsorption and the significance of this value is as follows: $n = 1$ (adsorption is linear); $n < 1$ (adsorption is a chemical process); and $n > 1$ (adsorption is a physical process). As seen from Table 2, the n value was found to be 3.959. For the present adsorption system, the value of n lie between 1 and 10, which indicates that the adsorption process was physical process [38]. The Langmuir maximum monolayer adsorption capacity (q_{max}) of the NZVI-CNS for copper ions was found to be 48.05 mg/g. The R_L value was used to predict the adsorption system,

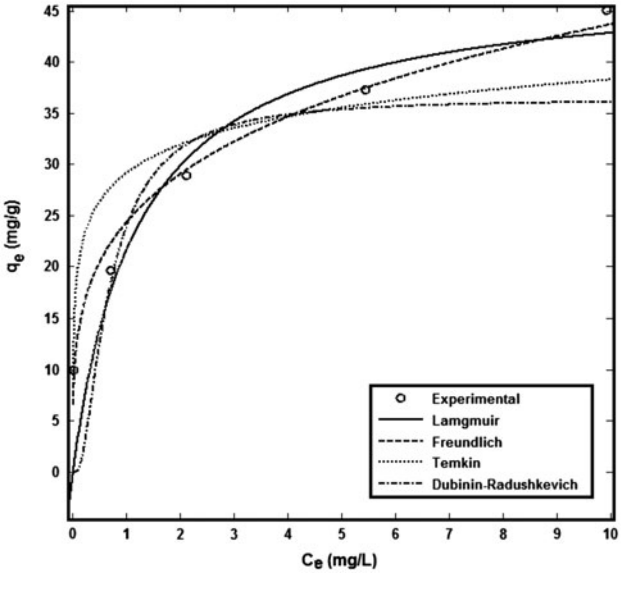

Fig. 11. Adsorption isotherm studies for the adsorption of copper ions by NZVI-CNS.

Table 2
Adsorption isotherm parameters for the removal of copper ions by the NZVI-CNS

Adsorption isotherm model	Parameters	Values	R^2
Langmuir	q_m (mg/g)	48.05	0.8542
	K_L (L/mg)	0.8268	
	SSE	112.4	
	RMSE	6.12	
Freundlich	K_F ((mg/g)(L/mg)$^{(1/n)}$)	24.43	0.9643
	n (g/L)	3.959	
	SSE	27.56	
	RMSE	3.031	
Temkin	A	1,636	0.8235
	B	1.713	
	b (kJ/mol)	1.471	
	SSE	136.1	
	RMSE	6.734	
Dubinin–Raduskevich	$q_{m,D}$ (mg/g)	36.4	0.7499
	β	2.569×10^{-8}	
	E (kJ/mol)	4.412	
	SSE	192.8	
	RMSE	6.943	

Table 3
Comparison of adsorption capacity of the adsorbents for the removal of copper ions

Adsorbents	q_m (mg/g)	References
Eucalyptus seeds	76.94	[43]
Wheat bran	51.5	[44]
Indian sal bark	51.4	[45]
NZVI-CNS	48.05	Present study
Coir pith	39.7	[46]
Carrot residues	32.74	[47]
Rice husk	31.85	[48]
Cork powder	15.6	[49]
Banana pith	13.46	[50]
Peanut husk	10.15	[51]
Raw eucalyptus seeds	7.401	[43]
Walnut shell	6.74	[52]
Hazelnut shell	6.65	[52]
Soya bean straw	5.44	[53]
Wheat straw	4.48	[53]
Walnut hull	4.04	[54]
Corn	3.78	[53]
Almond shell	3.62	[52]
Corn cob	2.18	[53]

and the significance of this value is as follows: $R_L = 0$ (irreversible); $0 < R_L < 1$ (favorable); $R_L = 1$ (linear); and $R_L > 1$ (unfavorable). The values of R_L calculated for the present adsorption system were in the range between 0 and 1, which indicates that the adsorption process was favorable [39]. The heat of adsorption (b) value for the present adsorption system was found to be less than 8 kJ/mol, which indicates the weak interaction between the copper ion and the NZVI-CNS. This indicates that the present adsorption system was a physical process [40]. The significance of mean free energy (E) value is <8 kJ/mol, physical adsorption [41]; $8 < E < 16$ kJ/mol, ion exchange [42]; and $20 < E < 40$ kJ/mol, chemisorption [41]. The estimated value of E for the present adsorption system was found to be less than 8 kJ/mol, which indicates that this study follows the physical adsorption process [41]. The order of best fit of adsorption isotherm models studied for the copper ions removal by NZVI-CNS was given on the basis of R^2 and error values: Freundlich > Langmuir > Temkin > Dubinin–Radushkevich isotherms. From this, it can be seen that the experimental data fitted well with the Freundlich model. The applicability of this model for the copper ions removal by NZVI-CNS indicated that the multilayer adsorption was held on the adsorbent surface under the studied experimental conditions. The maximum monolayer adsorption capacity (q_m) of the adsorbents for the removal copper ions is given in Table 3. From Table 3, it was observed that the NZVI-CNS examined in this research has a higher maximum monolayer adsorption capacity for the removal of copper ions from the aqueous solution.

The best-fitted adsorption isotherm model was used to design the batch adsorber for the removal of copper ions from the aqueous solution. The schematic view of the batch adsorber is shown in Fig. 12. The design objective of the adsorber was to measure the amount of adsorbent which was needed for treating the known volume and concentration of the copper ions from the aqueous solution at optimum condition. The mass balance over a batch adsorber is given as follows:

$$V\ (C_o - C_e) = M\ (q_e - q_o) \tag{23}$$

where V is the volume of copper ions solution (L), C_o is the initial copper ions concentration (mg/L), C_e is the copper ions concentration at equilibrium (mg/L), M is the mass of the adsorbent (g), q_e is the equilibrium adsorption capacity (mg/g), and q_o is the adsorption capacity at time $t = 0$ (mg/g). The fresh adsorbent was used for the present adsorption system, so the $q_o = 0$ and the Eq. (23) can be rewritten as follows:

$$M = \frac{(C_o - C_e)}{q_e}\ V \tag{24}$$

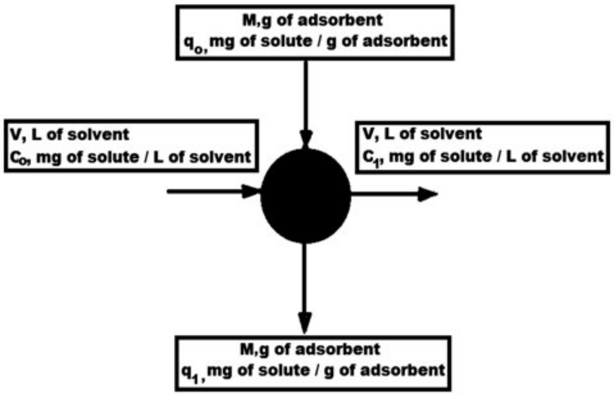

Fig. 12. A single-stage batch adsorber.

The best-fitted adsorption isotherm model for the present adsorption system was the Freundlich model. This model was included in the Eq. (24) and the equation can be rewritten as

$$M = \frac{(C_o - C_e)}{K_F\ C_e^{1/n}}\ V \tag{25}$$

The Eq. (25) relates the mass of adsorbent with the volume of the copper ion solution for the fixed initial copper ions concentrations. The adsorption isotherm data were fitted to the Eq. (25), and the results are shown in Fig. 13. For example, the amount of optimum adsorbent dose needed to treat the 10 L of the copper ions solution with 95% removal of 40 mg/L copper ions solution was found to be 13.05 g of adsorbent.

3.5. Adsorption kinetics and mechanism

The adsorption kinetic data were used to predict the adsorption rate and adsorption mechanism between the copper ions and NZVI-CNS. To examine the kinetics of the adsorption process, the various kinetic models such as pseudo-first-order [28] and pseudo-second-order [29] kinetic models were applied to the adsorption kinetic data. The pseudo-first-order constants, k_1 and q_e, cal, were estimated from the slope and intercept of the plot of log $(q_e - q_t)$ vs. t (Fig. 14(a)), and these values are presented in Table 4. The plot did not coverage well and which was deviated from the experimental data. This plot gives only lower coefficients of determination (R^2) values. Also, the q_e, cal, values much deviate from the q_e, exp, values. This indicates that the present adsorption system does not follow the pseudo-first-order kinetic model. Meanwhile, the adsorption kinetic data were applied to the pseudo-second-order kinetic model, and the experimental data converged very well with the excellent R^2 (>0.99) values. The pseudo-second-order constants, k_2, h, and q_e, cal, were estimated from the slope and intercept of the plot of t/q_t vs. t (Fig. 14(b)), and these values are given in Table 4. The results showed that the q_e, calculated from the pseudo-second-order kinetic model were in good agreement with the q_e, experimental values, which confirms the applicability

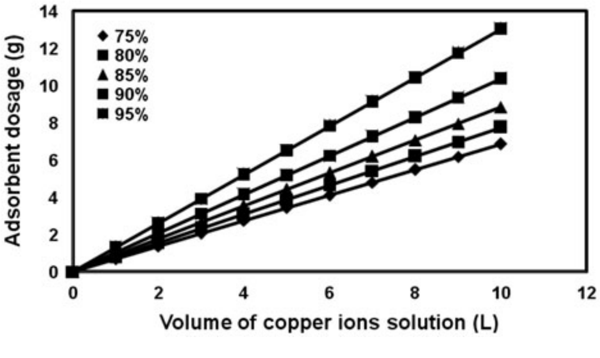

Fig. 13. Batch adsorber design for the removal of copper ions by NZVI-CNS.

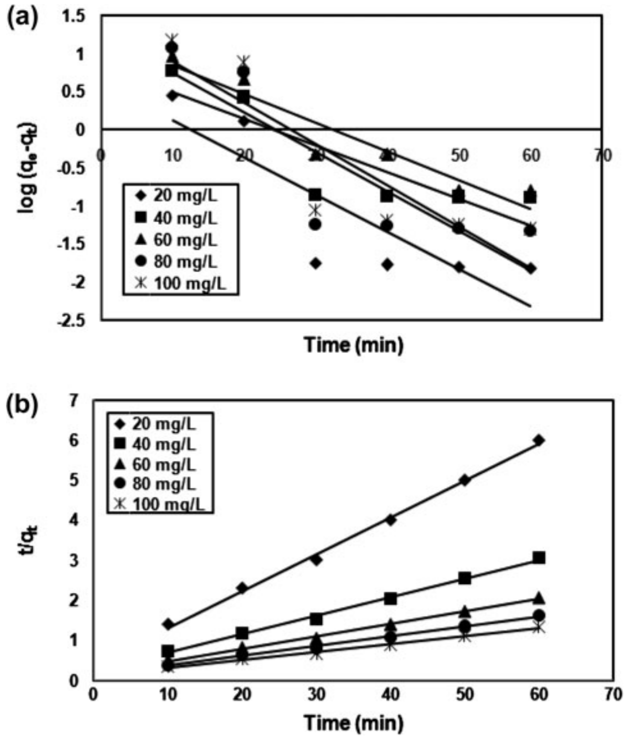

Fig. 14. Adsorption kinetic plots for the removal of copper ions by NZVI-CNS (copper ions concentration = 20–100 mg/L, volume of sample = 100 mL, solution pH = 6.0, adsorbent dose = 2 g/L, and temperature = 30˚C).

Table 4
Adsorption kinetic parameters for the removal of copper ions by NZVI-CNS

		Concentration of copper ions solution (mg/L)				
Adsorption models	Parameters	20	40	60	80	100
Pseudo-first-order kinetic equation	k_1 (min^{-1})	0.1105	0.0806	0.0852	0.1174	0.1243
	$q_{e,cal}$ (mg/g)	4.0457	6.9024	16.406	18.197	26.977
	R^2	0.724	0.721	0.893	0.727	0.764
	χ^2	2.934	2.841	5.623	2.678	3.241
Pseudo-second-order kinetic equation	k_2 (g/mg min)	0.0216	0.0099	0.0059	0.0046	0.0034
	$q_{e,cal}$ (mg/g)	10.869	21.739	32.258	41.667	51.282
	h (mg/g min)	2.551	4.7169	6.173	8.000	8.8496
	$q_{e,exp}$ (mg/g)	10.012	19.782	29.425	37.336	45.127
	R^2	0.997	0.996	0.996	0.995	0.994
	χ^2	0.0125	0.0221	0.0221	0.0232	0.0238

of this model for the present adsorption system. In addition to this, the Chi-square test was also carried out to check the best-fitted adsorption kinetic models. The lower Chi-square values were observed for the pseudo-second-order kinetic model than the pseudo-first-order kinetic model. This further confirms that the pseudo-second-order best fit the adsorption kinetic data for the removal of copper ions by NZVI-CNS. Based on the above observation, it can be concluded that the present adsorption system followed pseudo-second-order kinetic model.

Adsorption is a multi-step process which involves the movement of the copper ions from the aqueous solution to the adsorbent surface followed by diffusion through the boundary layer to the external surface of the solid adsorbent (film or external diffusion). Then, the adsorption occurs on the active sites of the solid adsorbent. Finally the copper ions passes through intraparticle diffusion (particle or internal diffusion) and adsorption occurs through pores within the solid adsorbent and aggregates. To identify the rate-controlling step in the adsorption process, the adsorption kinetic data were fitted to the different adsorption models such as intraparticle diffusion [30], Boyd kinetic [31], and shrinking core models [32–34]. Plotting q_t vs. $t^{1/2}$ should converge well and give a straight line that passes through the origin if the adsorption process is controlled by the intraparticle diffusion. The adsorption kinetic data were fitted to the intraparticle diffusion model, but they did not converge well and did not have straight lines that passed through the origin (Fig. 15(a)). This shows that the intraparticle diffusion is a part of the adsorption mechanism, but it is not only the rate-controlling step for the adsorption of copper ions onto the NZVI-CNS. The values of k_p and C were estimated from the slope and intercept of the plots of q_t vs. $t^{1/2}$ (Fig. 15(a)), and these values are listed in Table 5. The

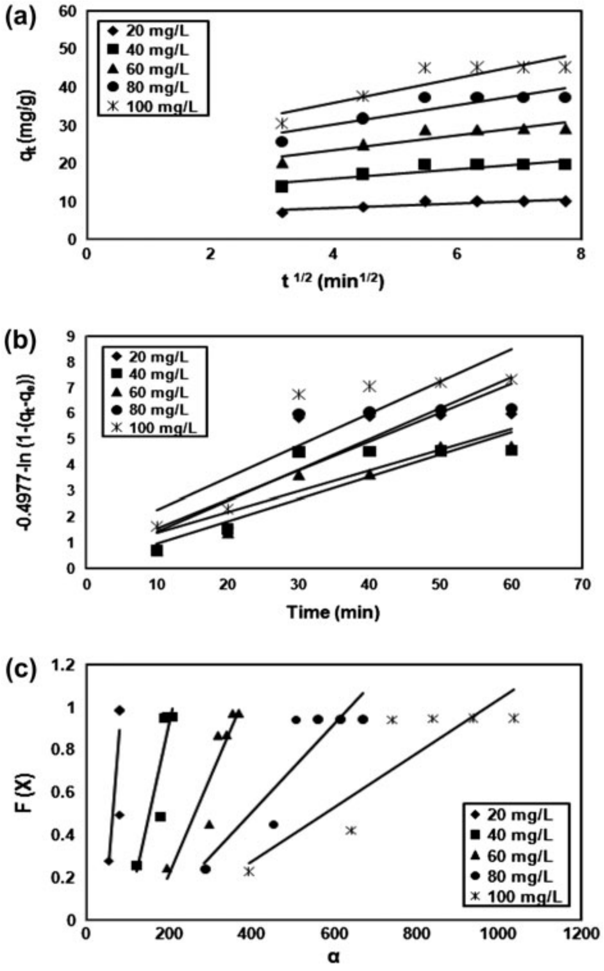

Fig. 15. Adsorption mechanism plots for the removal of copper ions by NZVI-CNS (copper ions concentration = 20–100 mg/L, volume of sample = 100 mL, solution pH = 6.0, adsorbent dose = 2 g/L, and temperature = 30˚C).

Table 5
Adsorption mechanism parameters for the removal of copper ions by NZVI-CNS

		Concentration of copper ions solution (mg/L)				
Adsorption models	Parameters	20	40	60	80	100
Intraparticle diffusion model	k_p (mg/g min$^{1/2}$)	0.597	1.239	1.964	2.527	3.240
	C (mg/g)	5.911	11.18	15.70	19.98	22.85
	R^2	0.784	0.779	0.813	0.788	0.795
	χ^2	0.0415	0.0339	0.0452	0.0422	0.0521
Boyd kinetic model	B	0.112	0.080	0.086	0.119	0.124
	D_i ($\times 10^{-12}$ m^2/s)	5.925	4.232	4.549	6.295	6.559
	R^2	0.724	0.721	0.893	0.727	0.764
SCM model	D ($\times 10^{-9}$ m^2/s)	2.2389	2.2883	2.2488	1.4377	0.8638
	R^2	0.624	0.798	0.868	0.817	0.800

two linear portions of the curve were obtained for the plot of q_t vs. $t^{1/2}$. This indicates the first linear portion was due to the film diffusion or external diffusion and the second linear portion was due to the particle diffusion or internal diffusion. The intercept C value gives an idea about the boundary layer effect on the adsorption of copper ions onto the NZVI-CNS. The larger the value of the intercept, the greater the contribution of the surface adsorption in the rate-controlling step. The actual slowest step in the adsorption of copper ions by NZVI-CNS was further explained by Boyd kinetic model. The adsorption kinetic data were fitted to Boyd kinetic model, and the results are shown in Fig. 15(b). From Fig. 15(b), it can be seen that the plots are linear but did not pass through the origin. This indicates the adsorption process was controlled by film or external diffusion. The effective diffusivity or effective diffusion coefficient (D_i) values were calculated using the Eq. (17), and the values are presented in Table 5. The effect of particle diffusion in the present adsorption system was further analyzed by fitting the adsorption kinetic data to the shrinking core model (Fig. 15(c)). From the results, it was observed that the particle diffusion may also affect the present adsorption system. The diffusivity (D) values were calculated using the Eq. (20), and the values are presented in Table 5. Finally, it was concluded that the both film and particle diffusion may control the adsorption of copper ions onto the NZVI-CNS.

4. Conclusion

This study investigated the adsorption behavior of NZVI-CNS for the removal of copper ions from the aqueous solution. The adsorption process was greatly influenced by the operating parameters such as solution pH, adsorbent dose, initial copper ions concentration, contact time, and temperature. These operating parameters were optimized for the maximum removal of copper ions. The values of thermodynamic parameters indicated that the adsorption process was feasible, spontaneous, and exothermic. The adsorption of copper ions onto the NZVI-CNS was well explained by the Freundlich adsorption isotherm model, whereas the kinetic study corresponds to a pseudo-second-order kinetic equation. The maximum monolayer adsorption capacity of 48.05 mg of copper ions/g of NZVI-CNS was obtained at an optimum condition. The adsorption process was controlled by both film and particle diffusion. A batch adsorber was designed for the known volume and concentration of copper ions solution. Finally, our results indicated that the NZVI-CNS materials can be prepared at low cost and these are environmentally friendly for the removal of copper ions, and similarly many other heavy metal ions, from water/wastewater.

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