Nanoscale Copper(II) Oxide: An Efficient and Reusable Adsorbent for Removal of Nickel (II) from Contaminated Water

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ABSTRACT

The present work describes the synthesis of copper(II) oxide nanoparticles (NPs) with high surface area (52.11 m²/g) and its Ni(II) adsorption efficiency from contaminated water at room temperature. Copper (II) oxide NPs are able to remove Ni(II) as 93.6 per cent and 93.7 per cent using 500 ppb & 1000 ppb initial concentration of nickel at near-neutral pH respectively. CuO NPs is very much effective to remove more than 75 per cent nickel over a wide range of pH even in presence of other competing ions like Cd^{2+}, Pb^{2+}, Cr^{6+}, SO_4^{2-}. Prepared CuO NPs can be used to remove Ni(II) from aqueous solution in real field application.

Keywords: Nickel(II); Copper(II) oxide NPs; Contaminated water; Removal; Adsorption

1. INTRODUCTION

Rapid expansion of industry and human population outburst are mainly responsible for water pollution. This creates scarcity of fresh water reservoir for drinking as well as irrigation purposes[1,3]. Dumping of untreated industrial and domestic waste containing inorganic compounds particularly heavy metal ions in water bodies causes water-borne diseases[2]. The heavy metals are highly toxic and exert adverse effects on the environment as they cannot be degraded by microorganisms[1,4,5]. Consumption of food contaminated with heavy metals depletes essential nutrients in human body causing several health disorders including cancer[6].

Among the ten heavy metals (led, arsenic, cadmium, chromium, cobalt, copper, mercury, manganese, zinc, and nickel which are of major public health concern) Ni^{2+} is one of the most hazardous metals[7]. It is the 5th most abundant element by weight of earth crust and released into water from minerals/ other sources[8]. Nickel and nickel compounds are widely used in metallurgical, chemical and food processing industries, especially as catalysts and pigments[9-12]. Nickel is also very important element for the synthesis of vitamin B_{12} in biological system but presence of its excess amount causes lungs cancer, bones problems and it may develop nausea, headache as well as dry cough[13-14]. The permissible limit of NI(II) is 0.02 mgL-1 (WHO/BIS) and 2.0 mgL⁻¹ for potable water and industrial wastewater respectively[12]. However, industrial wastewater of various industries contain nickel more than its present limit. Hence, treating waste water for removal of contaminants is essential to reduce their mobility within the terrestrial ecosystem[15]. Among the available removal techniques, adsorption is regarded as one of the most extensively used method because of simple design, low cost and no sludge formation[16,19-21]. Nanoscale metal oxides find applications as a cost efficient adsorbent in water treatment and remediation technology due to their small size and adsorption efficiency as compared to natural sized oxide[22]. CuO nanoparticle attracts great attention as an adsorbent to remove heavy metals from polluted water because of its high efficiency and low cost[18]. Ni(II) is most toxic than other valent state of same[23]. Consumption of nickel(II) contaminated water for drinking and other purposes leads to the various pathological problems[24]. Hence, Ni(II) is taken for whole experiment to be performed.

To the best of our knowledge, only few reports are available on the removal of Ni^{2+} using CuO nanoparticles18, but they have not tested the efficiency for real life contaminated water. The aim of our present work is to synthesise copper(II) oxide NPs through an easy, economic and environment friendly process and to explore its efficacy as a low-cost adsorbent for Ni^{2+} removal from contaminated water. The present study deals with synthesis and application of CuO nanoparticles to remove Ni(II) from contaminated water.

2. EXPERIMENTAL

2.1 Materials Involved

AR Grade chemicals e.g. Cupric Chloride (Merck), Hydrochloric acid (Merck), Sodium Hydroxide (Merck), capping agent polyethylene glycol (SRL), nickel chloride (Merck), acetone (Sigma Aldrich) and ethanol (Bengal chemicals) were used in the experiment. All experiments were performed using double distilled water.

2.2 Synthesis of Copper Oxide NPs

We have synthesised copper (II) oxide NPs by modifying our previously reported methods to get uniform desired particles[25]. A solution of 6.8 g $CuCl_2$, 3.2 g NaOH and 4 g of polyethylene glycol (Mol wt.~ 10000) capping agent mixture

in 500 mL ethanol were taken in a round bottom flask and refluxed at 75 ºC for 10 h. This was allowed to cool to room temperature. The mixture was again heated for 5 h at previous temperature and allowed to cool under room temperature. The obtained dark brown precipitate was centrifuged followed by washing with ethanol, acetone and warm water respectively. The above washing process was repeated at least 3 times to ensure no undesired contaminants present in the final products. The materials were heated at 120 ºC and cooled to room temperature for study.

2.3 Study for Batch Adsorption

Standard 1000 mgL^{-1} nickel solution was made by solubilising 2.21 g nickel chloride in 1000 mL water. The working solution of appropriate strength was prepared freshly from this standard solution by proper dilution. The adsorption study was performed by adding desired amount of CuO nano adsorbent into 100 mL of working Ni^{2+} solution of appropriate strength taken in a 250 mL conical flask. The mixture was shaken for 3 h on a mechanical shaker (IKA 400 *ic* control) at room temperature (25 ºC± 0.1 ºC) followed by centrifugation. The mother liquor was analysed for residual Ni^{2+} contaminant by Atomic Absorption Spectrophotometer. Batch experiments were performed to find out the effect of various parameters *viz.* adsorbent dose, presence of interfering ions, concentration of adsorbent and adsorbate, pH etc at room temperature.

The contaminant adsorbed was deduced using following equation

$$Q_e = \left(C_0 - C_e\right) \times V \ / W \tag{1}$$

Where, Q_e indicates adsorption efficiency (mgg^{-1}) in equilibrium state. C_0 and C_e represent initial and equilibrium concentrations of adsorbate [$Ni^{2+}(mgL^{-1})$] respectively; V (volume) and W (weight (g) of adsorbent).

Reusability of used CuO NPs was performed after carrying out the desorption study. For this purpose, a certain amount of Ni^{2+} solution (200 μgL^{-1} and 500 μgL^{-1}) were allowed to adsorb on CuO NPs. The nanoparticles were separated by filtration, washed repeated with dilute solution of acid/alkali and dried in air. The recovered CuO nanoparticles were reused for the adsorption study of the contaminants at room temperature. The process was repeated for several times to study the extent of reusability.

2.4 Characterisation of CuO NPs

Phase analysis and particle size of as prepared sample were carried out using an X-ray diffractometer (PW 1710, Philips, Holand) and Transmission Electron Microscope (CM 200, Phillips) respectively. Metal concentration in solution was analysed with Atomic Absorption Spectrometer (Model: AA 7000, LabIndia Pvt. Ltd).

3. FINDINGS AND DISCUSSIONS

Figure 1 shows X-ray diffraction (XRD) pattern of materials developed. It confirmed the formation of orthorhombic copper(II) oxide (JCPDS card no. 801268). Transmission electron microscopy (TEM) in Fig. 2 reveals the formation of CuO nanoparticles having diameter of 10-20 nm. Selected
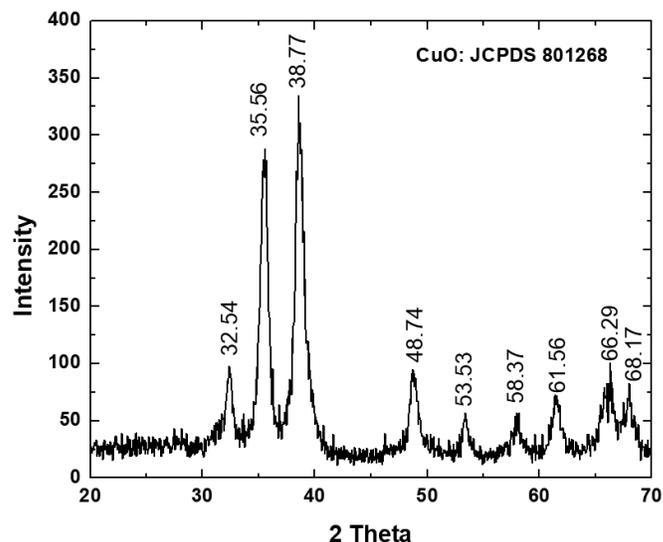

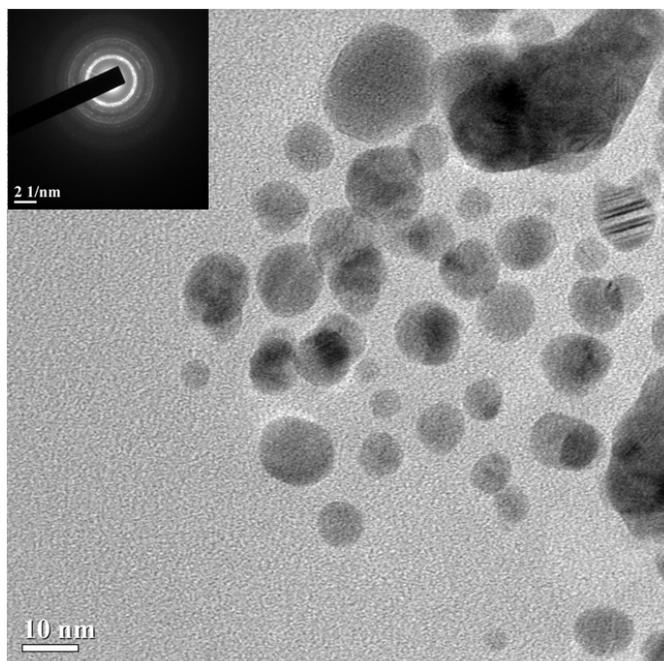**Figure 1. XRD of CuO nanoparticles.**

Figure 2. TEM and selected area electron diffraction (SAED) of CuO NPs.

area electron diffraction pattern (in the inset) also confirms the polycrystalline nature of CuO NPs. Elemental analysis of as prepared CuO also confirms the presence of Cu and O (Fig. 3). The specific surface area of the product as obtained from BET surface area analyser was found to be 52.58 m^2g^{-1}.

Fourier Transform Infrared Spectrophotometer (FTIR) is used to detect functional group present in the materials. The structural and bond information on a complex are available from FTIR and it is useful to study the strength and type of bonding[26]. Figure 4 showed the FTIR spectrum of the CuO BPs. The wavenumber of 2933 cm^{-1} and 3432 cm^{-1} clearly indicate different stretching mode of vibration of O-H bond. 523 cm^{-1} and 1011 cm^{-1} are Cu-O bending frequency 1639 cm^{-1} shows stretching frequency of Cu-O.
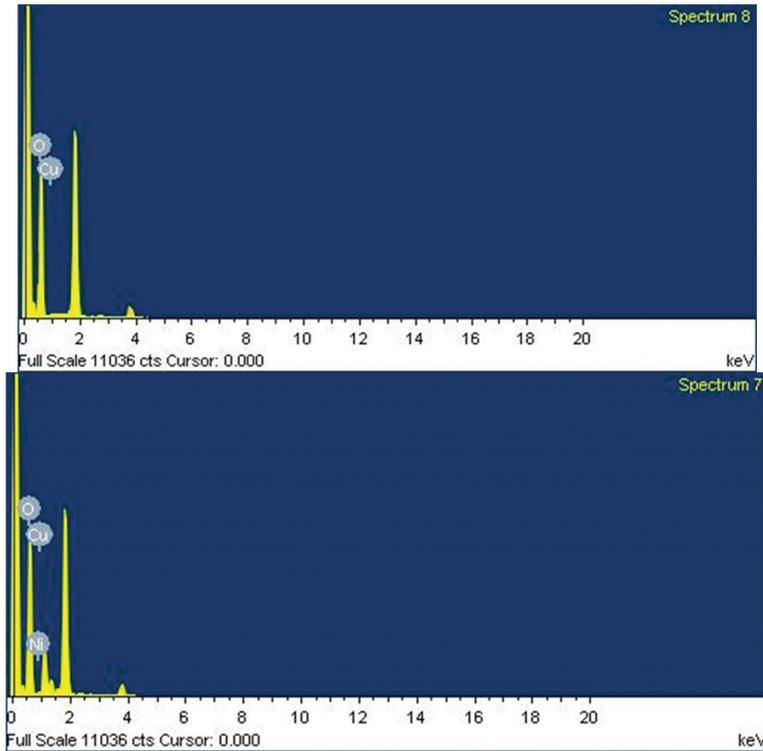
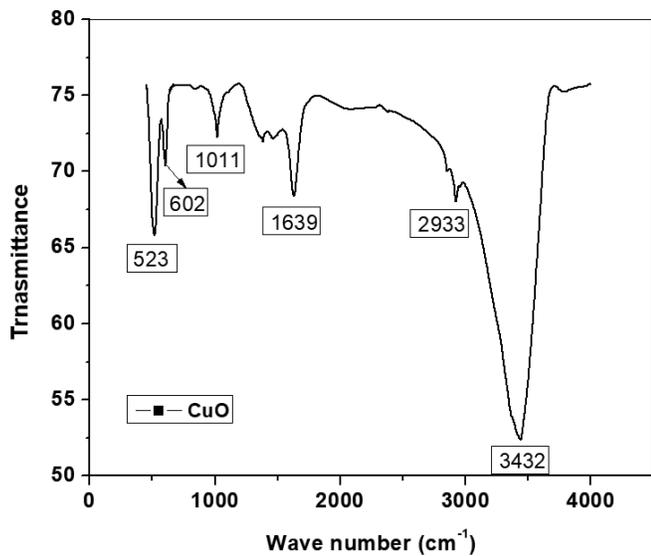Figure 3. EDX analysis of CuO NPs (A) and Ni(II) adsorbed CuO NPs (B).

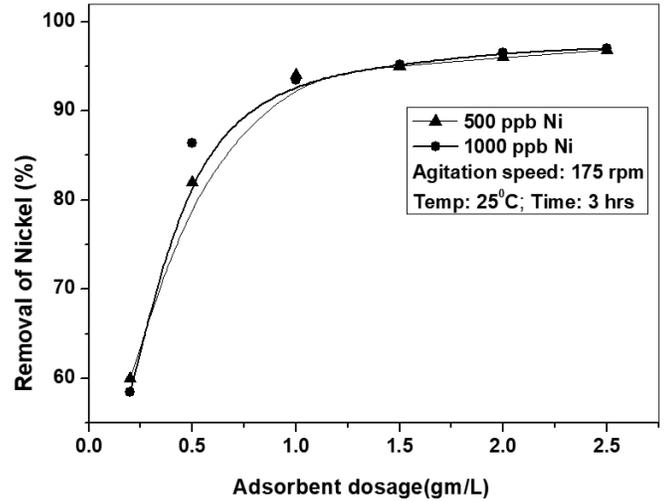Figure 4. FTIR spectrum of CuO NPs.

Figure 5. Variation of adsorbent dose on the removal of Nickel.
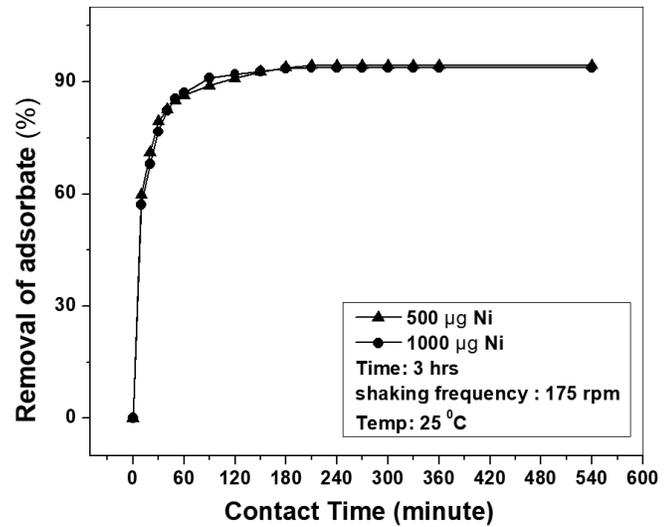
Figùre 6. Adsorption of Nickel Vs shaking time.
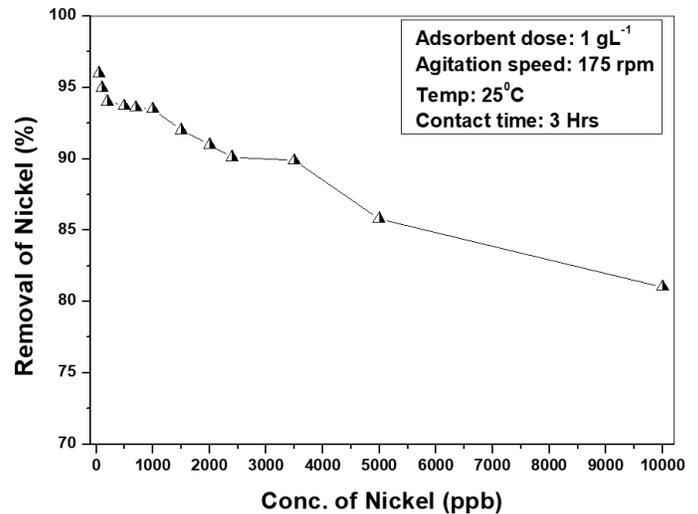
Figure 7. Variation of initial conc. of Nickel on the removal of Nickel.

3.1 Variation of Adsorbent Dosage

The variation of adsorbent dosage on batch adsorption of Ni(II) ion was carried out at room temperature using the amount of CuO from 0.1-2.5 gL^{-1} and is shown in Fig. 5. The per cent removal of nickel is significantly increased with sorbent dosage upto $1gL^{-1}$ and no significant increase is observed with further increase in adsorbent dose. This increasing adsorption with increase in adsorbent dose may be due to availability of active sites of adsorbent[27]. 1.0 gL^{-1} was benchmarked as optimum adsorbent dosage for entire study. Compared to other metal

Figure 8. Removal of nickel Vs initial pH of the working solution.
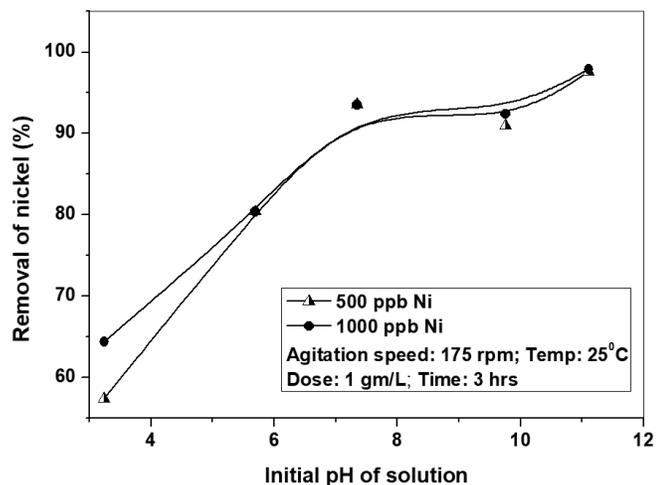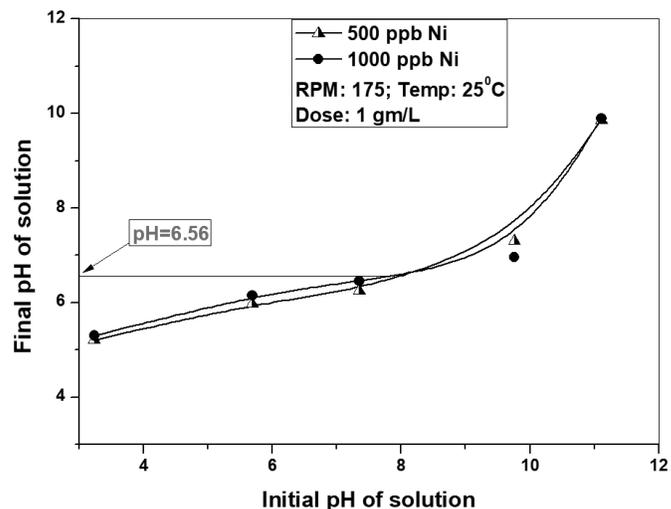

Figure 10. Plot of final pH with Initial pH of nickel solution.
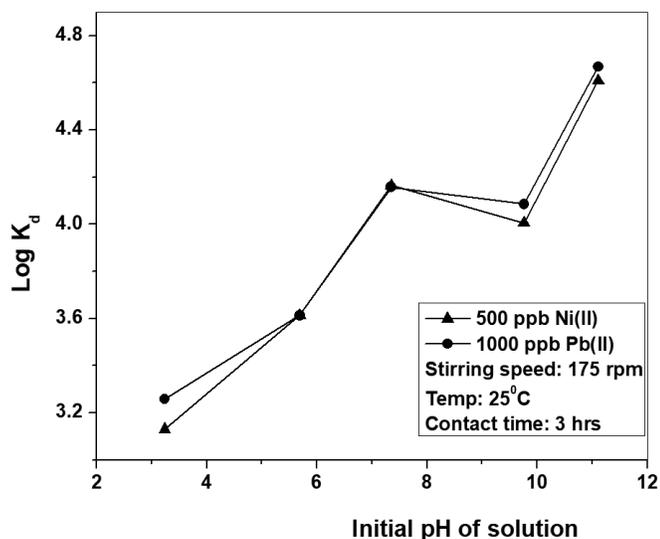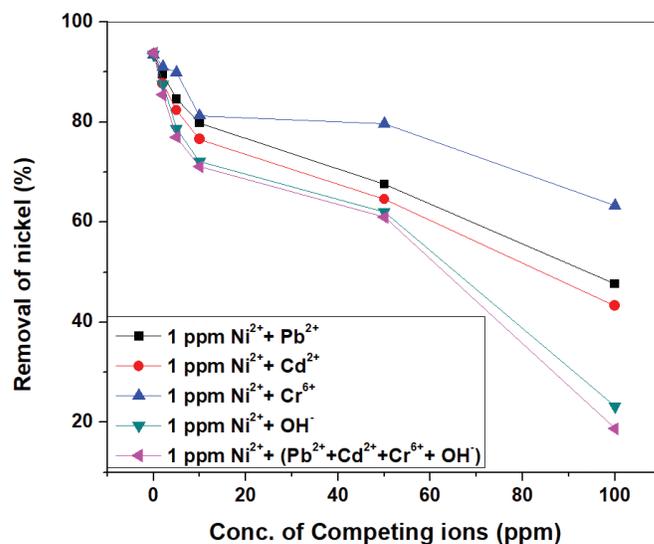

Figure 9. Log K_d Vs initial pH.

Figure 11. Effect of competing ions on removal of nickel.

oxide, CuO NPs is found to be effective for purifying water contaminated with nickel[28-29].

3.2 Variation of Shaking Time

Figure 6 revealed the per cent removal of Ni(II) with contact time keeping the amount of adsorbent at 1 gL[-1]. This clearly showed that the adsorption is very fast upto 1.5 hours. Thereafter, rate of adsorption become slow, finally reached equilibrium within 3 hours. No further noticable adsorption take place even increasing the contact time up to 9 hrs. Therefore, further adsorption experiments were conducted fixing shaking time of 3 hrs.

3.3 Variation of Adsorbate Initial Concentration

1 gL[-1] of copper oxide was mixed with mixed with different concentration (200-1000 ppb) of nickel solution, orbitally shaked for 3 h and results are given in Fig. 7. Initial rate of adsorption of nickel was fast and it diminished with

increase in adsorbate concentration. This may be due to the fact that the binding capacity of the adsorbate saturates at higher concentration of Ni(II) and as a result adsorption process slows down[30].

3.4 Effect of pH and Plausible Mechanism

Influence of pH on Ni(II) adsorption were examined at room temperature and the data are displayed in Fig. 8. It is clearly observed that Ni(II) adsorption on CuO NPs is sensitive to pH and optimum removal is achieved at pH 7.35. In order to comprehend binding ability of adsorbents with Ni(II) at various pH, it is required to determine the coefficient of distribution (K_d).

$$K_d = \left(\frac{Ci - Ce}{Ce} \right) \left(\frac{V}{M} \right) \qquad (2)$$

Ci and Ce are initial and equilibrium concentration respectively. The experimental K_d values are plotted as a

function of pH and evidenced in Fig. 9. It is noteworthy to mention that binding ability to specific pollutants increases with increase in K_d value[31]. Generally, K_d values of 10^3 mLg^{-1} and 10^4 mLg^{-1} are termed as good and outstanding respectively[32]. CuO NPs are found to be potential adsorbents of Ni(II) ions in water. The sharp increase of K_d with pH of CuO NPs indicates more sensitive nature of CuO to pH.

The effect of pH on adsorption was investigated by varying pH (2-11) without affecting other factors and evidenced in Fig. 8. More than 90 per cent removal of Ni was found at basic pH (9.0) and the removal was 70 per cent at acidic pH (4.3). The adsorption variation with pH can be envisaged considering Zero Point Charge (ZPC) of the adsorbent. To deduce ZPC of CuO NPs, initial pH *vs* final pH of working nickel solution is plotted and the findings are shown in Fig. 10. It reveals the neutral nature of CuO NPs at pH 6.56 (=ZPC) with the maximum sorption capacity of 9.35 mgg^{-1} at 25 °C.

Zero-Point Charge (ZPC) of CuO NPs was found to be at pH 6.56. So, it is neutral at pH 6.56. When batch adsorption (nickel solution/ CuO NPs) was performed in the pH range of 6.56 - 9.50, negative charge generated at reaction sites and positive charged contaminants like nickel are adsorbed well. However, at acidic medium (pH<7), adsorption decreased due to repulsion between cation and adsorbent surface. Thus, the mechanism of nickel removal follows mainly physical rather than chemical as evident from enthalpy (ΔH^0) calculation.

3.5 Adsorption in Presence of Competing Anions

The potable water is associated with some interfering ions *viz.* OH$^-$, Pb^{2+}, Cd^{2+} and Cr^{2+} which will practically compete with nickel ions during adsorption. Adsorption in presence of competing ions were experimented taking [Ni^{2+}]$_{initial}$ as 500 and 1000 ppb[33]. Other parameters *e.g.* shaking speed of 175 rpm, room temperature, pH 7.5 and agitation time of 3 hrs are fixed to get findings in Fig. 11. The decrease in the removal of nickel with increasing concentration of competing ions probably due to the competition/interference of same for the active sites on adsorbent surfaces. The factors responsible for decreased adsorption are concentration of competing ions, charge and size of same[34]. Hydroxide ion has more interfering effect than cadmium during adsorption. The removal efficiency diminished slowly after 20 ppm of hydroxide (−OH) ion and decreased sharply after 45 ppm of −OH ion. CuO get hydroxylated in presence higher concentration of hydroxide ion (>45 ppm) and no active sites are available for adsorption of contaminants. Thus, at basic pH, hydroxide ion is more preferably adsorbed compared to nickel. Probably, at higher pH formation of Cupric hydroxide is the reason of increased adsorption of hydroxide. Adsorption of nickel decreases profoundly in presence of the cadmium ion although it has almost same size and charge due to competing ion effect. It has been observed that mixed competing ion has most effect compared to individual ions. However, interfering ions were studied for batch adsorption in much higher concentration compared to same found in ground water. Hence, it may have inferenced that CuO NPs works as potential adsorbent of nickel from water in various pH and other ions.

3.6 Effect for Variation of Temperature and Thermodynamic study

The increase of nickel adsorption percentage with rise in temperature indicates the endothermic behaviour of adsorption. The thermodynamic parameters like entropy (ΔS^0), enthalpy (ΔH^0) and Gibbs free energy (ΔG^0)for the asorption of Ni(II) (using [Ni^{2+}]$_{initial}$ =500 µg/L) by CuO were determined by using the following equations[35]:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{3}$$

$$\log\left(\frac{q_e m}{Ce}\right) = \frac{\Delta S^0}{2.303R} + \frac{-\Delta H^0}{2.303RT} \tag{4a}$$

For unit adsorbent mass, Eq. (2a) became

$$\log\left(\frac{q_e}{Ce}\right) = \frac{\Delta S^0}{2.303R} + \frac{-\Delta H^0}{2.303RT} \tag{4b}$$

Where qe is nickel adsorbed per adsorbent mass (µg/g), C_e equilibrium conc. (µg/L), adsorbent weight m (g/L) and T (temperature). q_e/C_e is known as affinity of sorption

The temperature dependence of adsorption and its thermodynamic effects were studied at three different temperature viz. 298 K, 308 K, 318 K using initial [Ni^{2+}]=500 µg/L and summarised in Table 1. ΔH^0 and ΔS^0 were calculated from the plot of log(q_e/C_e) versus 1/T and ΔG^0 is determined applying Eq. (3). The positive values of ΔH^0 and ΔS^0 proves the endothermic nature of adsorption process and an increase in randomness at the solid–liquid interface. The decrease in ΔG^0 (Table 1) values with an increase in temperature indicates the spontaneous nature of the adsorption. Heats of chemisorption lies in between 80–200 kJmol^{-1}, ΔH^0 with value of 53.03 KJmol^{-1} clearly reveals physico-chemical nature of adsorption process instead of pure physical/ chemical one.

Table 1. Thermodynamics parameters determination

Temperature(K)	ΔH^0 (KJmol^{-1})	ΔS^0 (KJmol^{-1})	ΔG^0 (KJmol^{-1})
298			-6.57
308	53.03	0.20	-8.57
318			-10.57

3.7 Isotherms Analysis for Adsorption

The adsorption isotherms help immensely to understand the bonding/interaction among sorbate and sorbent at equilibrium. Langmuir and Freundlich isotherms models were followed to study adsorption phenomena for the removal of Ni(II) by CuO nanoparticles at 25 °C (Fig. 12).

The Langmuir equation assumes that adsorption is single layer phenomenon[36] and is expressed as follows:

$$Q_e = \frac{Q_m b C_e}{1 + b C_e}$$

or

$$\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \tag{5}$$

Where, Q_e: Quantity adsorbed (equilibrium, mgg^{-1}),

Q_m, Quantity adsorbed (Maximum, mgg^{-1}), C_e (mgL^{-1}), b: adsorption constant in equilibrium (Lmg^{-1}). Where, C_0 (mg/L) is the initial concentration of working nickel solution.

According to Freundlich isotherm, the adsorption is not restricted to monolayer and can be described in the following form[35]:

Figure 12. Equilibrium isotherm model for nickel adsorption.

$$Q_e = K_f C_e^{\frac{1}{n}}$$

or

$$\ln Q_e = \ln K_f + \frac{1}{n}\ln C_e \tag{6}$$

where, K_f (mg$^{1-1/n}$ L$^{1/n}$ g^{-1}) is Freundlich constant. n is related to sorption intensity of the CuO NPs. b is 9.53 mg of Ni ions adsorbed per gram of CuO NPs (Eqn 5). The value of K_f calculated was found to be 39.374 mg$^{1-1/n}$ L$^{1/n}$ g^{-1}. The equilibrium adsorption data fitted better to Langmuir isotherm (R^2=0.9932) as compared to Freundlich isotherm (R^2=0.9809). Therefore, the adsorption Ni(II) by CuO nanoparticles is mainly confined to the monolayer.

3.9 Nickel Desorption Study

For regeneration study adsorbed copper Oxide nanoparticles were taken and regenerated using dilute hydrochloric acid/ sodium hydroxide[38] at room temperature. 0.2 (M) and 0.5 (M) of dilute acid/alkali were used in the experiment. Adsorbed nickel ion desorbed in presence of acid/alkali to make CuO reusable for adsorption purposes. From Table 2 it is obvious that HCl is superior eluent with 81 per cent desorption efficiency compared to NaOH (64 %).
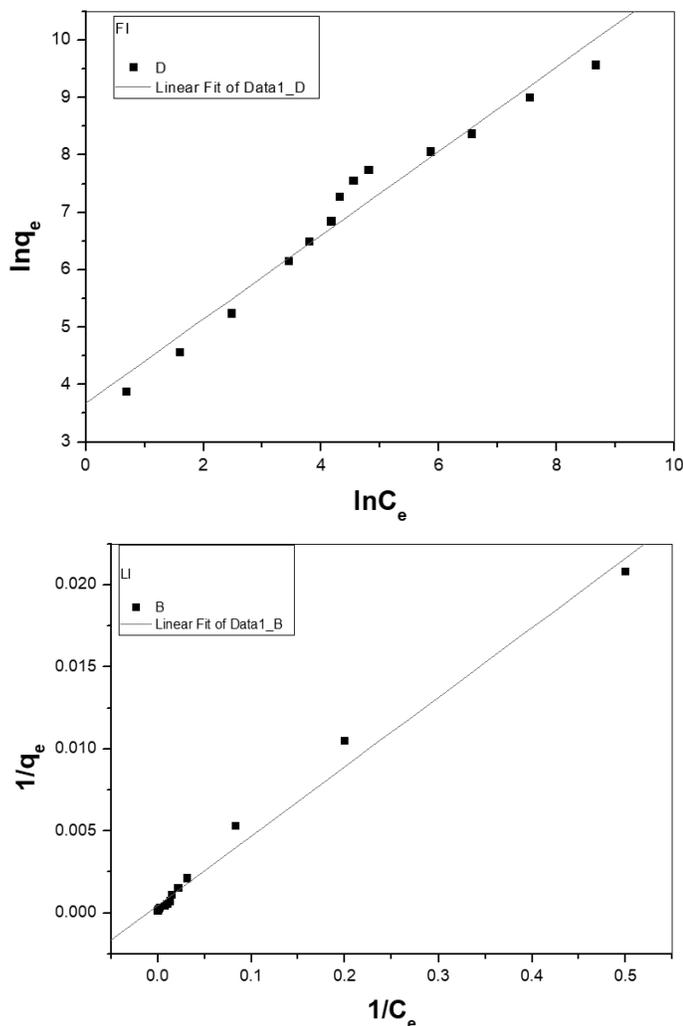
4. LEACHING STUDY

According to literature reports CuO NPs are not so much toxic in air, but in liquid they may become toxic after ingestion[39-40]. Therefore, we have filtered the solution containing CuO and carefully examined the filtrate using Atomic Absorption Spectrophotometer. The result reveals that no/trace amount of Cu(II) are present in the filtrate. Solutions remained after each adsorption studies have been analysed for determination of Cu(II) and no copper is found in the solution. So, the analysis of solution after adsorption confirms no leaching of Cu(II) in water (Table 3)

5. CONCLUSION

- CuO NPs were prepared through economic, easy process and the particles reveals as excellent candidates for decontamination of Ni(II) from water.
- From environmental application point of view, CuO is a

Table 2. Desorption study

Ni(II) mgL^{-1}	Acid/alkali used	Conc (M)	Ni(II) after adsorption (mgL^{-1})	Regenerated CuO (%)
500	Sodium hydroxide	0.20	290	58
500	Sodium hydroxide	0.50	320	64
500	Hydrochloric acid	0.20	410	81
500	Hydrochloric acid	0.50	478	95.6, Soluble
1000	Sodium hydroxide	0.20	560	56
1000	Sodium hydroxide	0.50	632	63.3
1000	Hydrochloric acid	0.20	768	76.8
1000	Hydrochloric acid	0.50	949	94.9, soluble

Table 3. leaching study (adsorbent dosage: 1 gL⁻¹)

Filtrates taken after interval (min)	Conc of Cu(II) in eluent after adsorption (mgL⁻¹)
0	trace
10	trace
20	trace
30	trace
60	trace
90	trace
120	trace
150	trace
180	trace

cheap, promising and effective adsorbent over a pH range (from 5.5 to 11) in presence of other competing/interfering ions. The adsorbent is less sensitive to pH and may be acceptable for cleaning up industrial effluents, especially effluents having low pH.

- Heats of chemisorption generally fall into a range of 80–200 kJmol⁻¹, ΔH^0 with value of 53.03 KJmol⁻¹ clearly reveals physico-chemical nature of adsorption process instead of pure physical/ chemical one.
- Equilibrium sorption data reveals that the adsorption is multi-layered on the heterogeneous adsorbent surface. The optimum uptake capacity of adsorbent is found to be 9.53 mgg⁻¹ for nickel at RT.
- Desorption study finds spent adsorbent to be regenerated upto 81 per cent with dilute acid/alkalis and may be used for multiple times.

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