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Application of nanobiocomposite hydrogel modified by TETA and β-cyclodextrin for the removal of Ni(II) ions from aqueous environment

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ABSTRACT

The present study was carried out using a nanobiocomposite hydrogel (NBC) modified by triethylene tetra amine (TETA-NBC) and β-cyclodextrin (CD-NBC) as an adsorbent for the removal of Ni(II) ions from aqueous environments. Experiments on optimization of parameters viz., pH, contact time, temperature, initial Ni(II) concentration and adsorbent dosage were conducted in a batch scale. Under optimized conditions maximum Ni(II) removal was noted as 99.34% and 87.43% in the case of TETA-NBC and CD-NBC respectively. Mode of adsorption was evaluated using equilibrium and kinetic studies. Equilibrium studies suggested a homogeneous mode of Ni(II) adsorption. Better applicability of pseudo-first order kinetic model suggested physisorption as the underlying phenomena. Thermodynamic studies showed that adsorption process was endothermic and spontaneous in nature. The mechanism of adsorption by TETA-NBC and CD-NBC was elucidated using FT-IR, SEM and EDX analyses.

Keywords: Adsorption, hydrogel, nanobiocomposites, chitosan (Ch), polyaniline NPs (PANI), nickel(II).

INTRODUCTION

In recent years, the increased use of heavy metals has resulted in a massive flux of the metallic substances in the environment. The metals are of special concern due to their persistency and recalcitrant properties in nature [1]. Among the heavy metals, nickel is of special interest because of its widespread presence in industrial applications such as nickel-cadmium batteries, electroplating, plastic manufacturing, mining and metallurgical, plastics manufacturing, fertilizers, porcelain enameling, steam electric power plants etc. [2,3]. According to WHO guidelines, the maximum permissible limit of nickel in industrial effluent is 4.1 mg/L and less than 0.1 mg/L in drinking water [4]. Nickel(II) is reported as a potent carcinogen since exposure to high concentration of nickel causes cancer of bones, stomach, lungs and nose [5]. Acute nickel poisoning causes dermatitis, dizziness, headache, vomiting, nausea, cyanosis, chest pain, dry cough, rapid respiration and extreme weakness [6,7]. In sight of toxic effects on human and animal life due to nickel contamination, it is necessary to treat nickel bearing industrial effluents prior to its discharge into the receiving water bodies.

Over the past few decades, the main methods used for the treatment of nickel(II) bearing wastewaters include precipitation, coagulation, evaporation, ion exchange, membrane processing, adsorption and solvent extraction [8]. Among the various remediation methods, adsorption is widely applied since it offers an attractive and cost effective remediation option and has significant benefit [9]. Effective adsorbents and simple technologies are still in great demand to remove heavy metal ions from aqueous environments.

Nanobiocomposites which incorporates the advantageous properties of both biopolymers and nanoparticles have recently received an increasing attention as a potential adsorbent in reducing metal concentration present in industrial effluents [10]. Nanoparticles are considered as one of the important building blocks in fabrication of nanomaterials due to their basic properties such as high surface area to volume ratio and small size. Moreover, their extremely small size provides better kinetics for the adsorption of metal ions from aqueous environments [11, 12]. Chitosan which is known to be obtained from chitin as a deacetylated product has been reported as a potential biopolymer for the removal of metal ions from aqueous environments due to the presence of hydroxyl and amino functional groups [13]. Gum Arabic is a complex arabinogalactan which comprises a small proportion of proteinaceous materials and has been widely used in removal of metal ions [14]. Clay minerals such as montmorillonite (MMT) recently has gained much attention for the removal of pollutants due to its high cation exchange capacity and adsorption capacity, expansion properties as well as layered structure, high surface area, low cost and abundance [15, 16, 17]. Polyaniline (PANI) because of their well-defined electrochemical properties, low cost, easy polymerization, high environmental stability and variety of nanostructured morphologies itis considered as one of the promising polymers [18]. Recently, some researches have been directed towards the application of polyaniline and its composites for environmental applications based on the chelating properties of electron donating groups such as amine and secondary amino groups present on the polyaniline polymers [19]. Recent reports suggested that modified form of nanobiocomposites are used for an enhanced removal of metal ions. Triethylene tetra amine (TETA)and β-cyclodextrin (CD) has been reported to render amine and hydroxyl functional group respectively which are known to remove heavy metals via strong interactions or surface complexation [20,21].

The purpose of the present work is to investigate the adsorption of Ni(II) ions onto a potential nanobiocomposite hydrogel composed of chitosan, gum Arabic, montmorillonite and polyaniline nanoparticles crosslinked via glutaraldehyde and further modified by triethylene tetra amine (TETA) and β-cyclodextrin. The process was optimized and adsorption isotherms and kinetics models were studied to describe the experimental data. The adsorption mechanism of Ni(II) onto the modified nanobiocomposite hydrogel was further elucidated using FT-IR, SEM and EDX analyses.

MATERIALS AND METHODS

Chemicals

All the chemicals used in this present study including cetyltrimethylammonium bromide (CTAB), aniline, ammonium persulfate (APS), plant gum (gum Arabic), montmorillonite (MMT), glutaraldehyde, glacial acetic acid, triethylene tetra amine (TETA) and β-cyclodextrin (CD), $Ni(NO_3)_2.6H_2O$, NaOH, HCl and ethanol were purchased from Sigma Aldrich, India and were used without further purification.

Synthesis of polyaniline nanoparticles

Polyaniline nanoparticles were synthesized following a formerly described process [22] using CTAB as a surfactant. In this procedure, 40mL of CTAB (0.5 M) solution was prepared to which 1 mL of aniline monomer was added dropwise. Further to the above solution, 22g of HCl (1.5 M) and 1.23g of APS were added and polymerization of the mixture was allowed by vigorous stirring at 3°C for three hours. At the end of polymerization reaction, the product was washed with distilled water and ethanol to remove unreacted fraction. The polyaniline nanoparticles were retrieved and dried in hot air oven at 40°C.

Preparation and characterization of nanobiocomposite hydrogel (NBC)

The nanobiocomposite hydrogel used in this study was prepared following a previously described procedure [23] with minor modifications. A suspension of montmorillonite (3%) in water containing 2% glacial acetic acid was prepared to which the prepared polyaniline nanoparticles were dispensed to this suspension and was stirred under magnetic conditions for 2 hours. Prior dissolution of gum Arabic (2%) in de-ionized water was carried out by heating upto a temperature of 60°C. The solution was further cooled and added to the above suspension which was later divided into two parts as solutions A and B. Triethylene tetra amine (5% v/v) was added to the solution A whereas β-cyclodextrin (0.1 %) was added to the solution B. Finally, to both the solutions chitosan (3%) was slowly added under stirring conditions until a slurry was formed after which glutaraldehyde (2% v/v) was added to form a thick hydrogel. The hydrogel was frozen at 4°C for 2 hours after which it was immediately thawed at 70°C for 10 minutes. This process of freezing and thawing was repeated upto 3 times after which the nanobiocomposite hydrogel was dried and powdered.

The BET surface area of the nanobiocomposite hydrogel (NBC) was calculated following the standard procedure [24]. Thermogravimetric analysis (TGA) of the NBCs was carried out under high purity helium supplied at a purge gas flow rate of 0-1000 mL/min (Diamond TG/DTA, Perkin Elmer, USA) in the temperature range of 20-650 °C at a heating rate of 20 °C min^{-1}.

Batch adsorption studies

In the present study**,** effect of parameters viz., pH (2-10), contact time (2-24h), temperature (10-50°C), initial Ni(II) concentration (100-600 mg/L) and adsorbent dosage (0.2-1.2 g/L) on the removal efficiency of Ni(II) were studied in batch mode. The experiments were conducted in 250 mL Erlenmeyer flasks containing 100 mL of Ni(II) test solution under continuous shaking condition at 120 rpm. At the end of agitation time, the samples were withdrawn and subjected to centrifugation at 8,000 rpm for 10 min. The residual Ni(II) concentration present in the supernatant was analyzed using an atomic adsorption spectrophotometer (AAS). The adsorption capacity (q_e) and the removal percentage (R%) of Ni(II) were calculated according to the following equations:

$$q_e = \frac{C_0 - C_e}{M} \times V \qquad (1)$$

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \qquad (2)$$

where q_e (mg/g) is the uptake of metal ion on the adsorbent, C_0 and C_e are the initial and equilibrium concentration of metal ions in the residual solution (mg/L), V is the volume (L) of metal ion solution used and M is the mass (g) of the adsorbent used.

Equilibrium, kinetic and thermodynamic studies

The equilibrium data were analyzed using two parameter isotherms-Langmuir [25], Freundlich [26] and Dubinin-Radushkevich (D-R) [27]. The significance of the model was tested by their correlation coefficients and average percentage errors values. Kinetic experiments were conducted under optimized conditions and samples were withdrawn at regular intervals of time. To understand the mode and rate of adsorption process, various kinetic models viz., pseudo-first order [28], pseudo-second order [29], intra-particle diffusion model and Boyd plot [30] were used.

Thermodynamic studies were conducted by estimating the uptake values at a temperature range of 10-50°C. The Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) are the three fundamental thermodynamic parameters with respect to the heat requirements and randomness of the process and were obtained using the standard equations [31].

Instrumental analysis

Fourier transformed infrared spectra were recorded on an Avatar 330 model (Thermo Nicolet Co., USA) FT-IR spectrometer. For FT-IR studies, 5 mg of adsorbent both before and after Ni(II) adsorption was encapsulated in 400 mg of KBr translucent discs which were obtained by pressing the ground material with the aid of a bench press. Each experiment was repeated at least twice, both producing good results.

The surface morphology of both TETA-NBC and CD-NBC before and after adsorption of Ni(II) ions was analyzed using scanning electron microscopy (SEM) (Stereo Scan LEO, Model-400). EDX analysis were conducted using Noran System Six model Energy Dispersive X-Ray Microanalysis System (Thermo Electron Corporation, Japan) attached to SEM. Accelerating voltage was kept constant at 15 kV, to facilitate the emission of secondary X-rays.

RESULTS AND DISCUSSION

Characterization of the nanobiocomposite hydrogel

The modified nanobiocomposite hydrogels were characterized for its adsorption potential. The BET surface area of TETA-NBC and CD-NBC was found to be 0.89 m^2/g and 0.38 m^2/g respectively. Thermogravimetric analysis (TGA) plays an important role in determining the thermal stability of the nanobiocomposite. Thermogravimetric analysis suggested a lower weight loss percentage in case of TETA-NBC (30.5%) as compared to CD-NBC (54.3%) which suggested an enhanced crosslinking in case of TETA-NBC than CD-NBC. X-ray diffraction (XRD) analysis confirmed the presence of polyaniline nanoparticles on the nanobiocomposite surface (Figure not shown). The average particle/aggregate size was calculated to be 4.18 nm as per Debye-Scherrer equation.

Effect of parameters

The effect of pH on the removal of Ni(II) was examined over the range of 2 to 10 and is represented in Fig.1(a). Result indicated that on increasing the pH of nickel solution, the Ni(II) removal also showed an increasing trend for both TETA-NBC and CD-NBC which can be attributed to the fact that with the increase in pH, the number of negatively charged sites on the surface of the nanobiocomposite hydrogel also increased [9]. The sorption of Ni(II) reached equilibrium at pH 6.0 in case of both TETA-NBC and CD-NBC. Lower percentage of Ni(II) removal at acidic pH might be due to the competition which occurs between positively charged Ni(II) ions and hydrogen ions for the metal binding sites present on the surface of the nanobiocomposite [32].

Nickel(II) removal by both TETA-NBC and CD-NBC as function of contact time (2-24 h) is represented in Fig.1(b). The Ni(II) removal efficiency of TETA-NBC and CD-NBC reached equilibrium at 10 h and 16 h respectively. The Ni(II) removal efficiencies of both the nanobiocomposite hydrogels increased rapidly at initial stages due to the availability of large number of active sites on the surface of nanobiocomposite which could result in efficient binding of the metal ions. With gradual occupancy of the active sites, the sorption become less efficient in the later stages due to the repulsion between metal ions present in the solution and metal ions adsorbed on the surface of the nanobiocomposite hydrogels [33].

The effect of temperature on the removal of Ni(II) was studied in the range of 10-50°C. Maximum Ni(II) removal was obtained at 40°C in case of both TETA-NBC and CD-NBC and is represented in (Fig.1(c)). This could be attributed to the fact that with an increase in temperature, swelling occurs within the surface of the nanobiocomposite hydrogels thereby enabling more metal ions to penetrate further [34].

The effect of initial Ni(II) concentration on the removal efficiency of both TETA-NBC and CD-NBC was investigated by varying the Ni(II) concentration from 100 mg/L to 600 mg/L (Fig.1(d)). It was noted that the maximum Ni(II) removal was found to occur at the concentration of 400 mg/L in case of both TETA-NBC and CD-NBC. An increase in the removal of Ni(II) was noted along with increase in initial metal concentration due to the availability of sufficient amount of Ni(II) ions for the sorption process. However, an improvement in the uptake of Ni(II) was not observed with further increase in the Ni(II) concentration due to the possible saturation of the active sites present on the nanobiocomposite hydrogels [35].

The dependence of Ni(II) removal on the adsorbent dosage was studied by varying the NBC dosage from 0.2 to 1.2 g/L while keeping all the other parameters constant. As shown in Fig.1(e), TETA-NBC exhibited highest removal at a dosage of 0.8 g/L followed by CD-NBC (1.0 g/L). An increase in the removal efficiency of Ni(II) was noted along with the increase in adsorbent dosage which could be due to the presence of increased number of sites and exchangeable ions for metal adsorption. However, beyond the optimum dosage, a decreasing trend in the removal of Ni(II) was observed due to the clumping of the material therefore decreasing the leaching of the pollutant in water [30].

Therefore, the maximum removal of Ni(II) by TETA-NBC and CD-NBC was found to be 99.34% and 87.43% respectively under optimized condition in batch mode.

Equilibrium, kinetic and thermodynamic studies

Various two parameter isotherms (Langmuir, Freundlich and Dubinin-Radushkevich (D-R)) were employed for fitting the equilibrium data in order to examine the relationship between the metal adsorbed on the adsorbent surface and the metal present in the residual solution. The isotherm constants, correlation coefficient values (R^2) and average percentage error values (APE%) were calculated and presented in Table 1. Langmuir model was found to exhibit the best fit among the various isotherm model tested in case of both TETA-NBC and CD-NBC as shown in Fig.2(a) owing to their low APE values and high R^2 values thereby suggesting a homogeneous monolayer mode of Ni(II) adsorption. The results of the present study also indicated that the Freundlich model exhibited a poor fit showing low R^2 values and high APE values. The data on mean free energy (E) from D-R isotherm model suggested that a higher amount of energy is required for the removal of Ni(II) from TETA-NBC when compared to CD-NBC thereby confirming a higher affinity between Ni(II) and TETA-NBC.

In order to understand the nature of the adsorption process, various kinetic models (pseudo first order, pseudo second order, intra-particle diffusion and Boyd plot) were evaluated. Various kinetic parameter constants are presented in Table 1. In the present case, the results suggested that pseudo first order model exhibited the best fit among all the models for both TETA-NBC and CD-NBC owing to their high R^2 values and low APE values thereby indicating physisorption as underlying phenomena for the adsorption process (Fig.2(b)). The intraparticle diffusion coefficient for the adsorption of Ni(II) onto TETA-NBC and CD-NBC were calculated from the slope of the plot between the amount of Ni(II) adsorbed q_t (mg/g) vs $t^{0.5}$ (min) as shown in Fig.2(c). High R^2 values and low APE values for intraparticle diffusion model signified the validation of the model (Table 1). The kinetic data were further analyzed using Boyd plot to check whether the sorption proceeds via film diffusion or intraparticle diffusion mechanism. In the present study, the plot was found to be linear but did not pass through the origin (Fig.2(d)) which clearly indicated that both film diffusion and intraparticle diffusion played a role in the adsorption process.

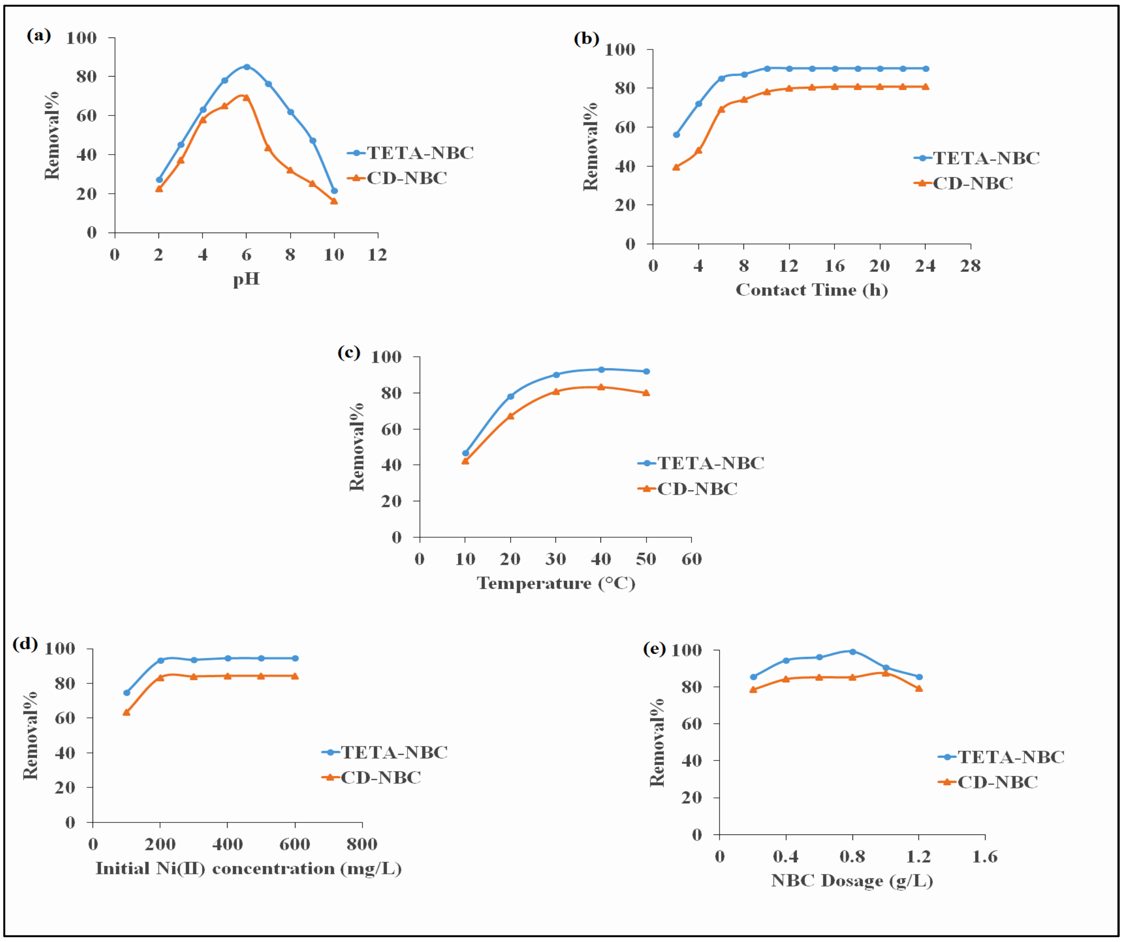

Fig 1: Effect of (a) pH (b) contact time (c) temperature (d) initial Ni(II) concentration (e) adsorbent dosage on Ni(II) removal (%) by TETA-NBC and CD-NBC

Table 1: Equilibrium isotherm model and kinetic model parameters for Ni(II) adsorption on TETA-NBC and CD-NBC

Isotherm models	Parameters	TETA-NBC	CD-NBC
Langmuir	q_m (mg/g)	208.33	135.13
	K_L (L/mg)	0.04	0.11
	R^2	0.98	0.95
	APE (%)	1.56	9.52
Freundlich	K_F (mg/g)	13.58	38.57
	n	1.35	1.30
	R^2	0.72	0.86
	APE (%)	20.49	18.59
Dubinin–Radushkevich	q_m (mg/g)	392.28	286.37
	β (mol^2/J^2)	$2*10^{-6}$	$3*10^{-6}$
	E (kJ/mol)	0.50	0.40
	R^2	0.97	0.99
	APE (%)	5.54	6.39
Kinetic models			
Pseudo first order	q_e (mg/g)	517.72	504.77
	K_1 (min^{-1})	0.13	0.15
	R^2	0.99	0.96
	APE(%)	1.44	1.91
Pseudo second order	q_e (mg/g)	270.27	666.66
	K_2 (g/mg/min)	$1.66*10^{-3}$	$8.85*10^{-5}$
	R^2	0.94	0.90
	APE(%)	11.89	5.43
Intraparticle diffusion	V	135.42	77.38
	C	51.65	20.23
	R^2	0.98	0.95
	APE(%)	2.53	5.26

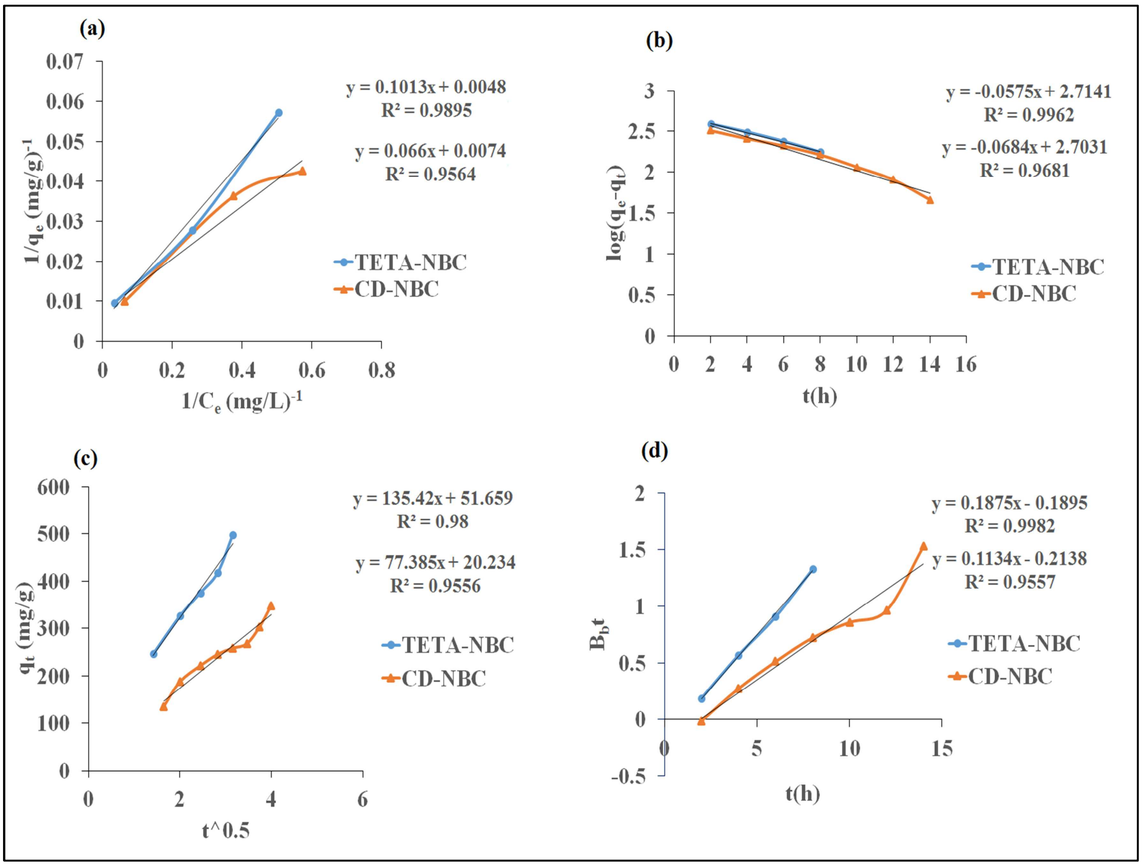

Fig 2: (a) Langmuir isotherm (b) Pseudo first order kinetics (c) Intraparticle diffusion (d) Boyd plot of Ni(II) adsorption onto TETA-NBC and CD-NBC

In order to describe the thermodynamic behavior of adsorption of Ni(II) onto modified nanobiocomposite hydrogels, thermodynamic parameters (Δ*G*, ΔH, Δ*S*) were calculated from standard equations and are presented in Table 2. The process was found to be spontaneous with the increase in temperature which was indicated by negative values of the standard Gibb's free energy (ΔG) and maximum spontaneity was noted at 40°C in both the cases. The values of ΔH and ΔS were calculated from the slope and intercept of the plot of (q_e/C_e) vs1/T (Fig. 3). The positive values of the standard enthalpy (ΔH) indicated the adsorption as an endothermic process or heat absorbing in nature. The positive values of standard entropy (Δ*S*) suggested an increase in randomness at the solid/solution interface during the adsorption of Ni(II) on the nanobiocomposite hydrogels.

Table 2: Thermodynamics parameters

NBCs	Temperature (K)	ΔH° (kJ/mol)	ΔS° (kJ/mol/K)	ΔG° (kJ/mol)
TETA-NBC	283	+26.66	+0.099	-1.357
	293			-2.347
	303			-3.337
	313			-4.327
CD-NBC	283	+61.69	+0.211	1.977
	293			-0.133
	303			-2.243
	313			-4.353

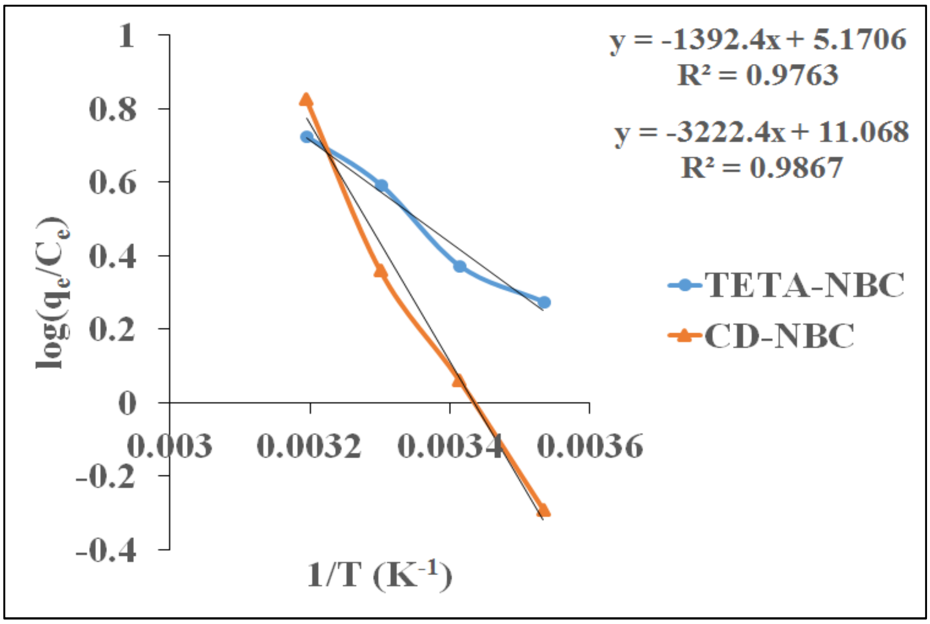

Fig 3: Thermodynamic studies for adsorption of Ni(II) on TETA-NBC and CD-NBC

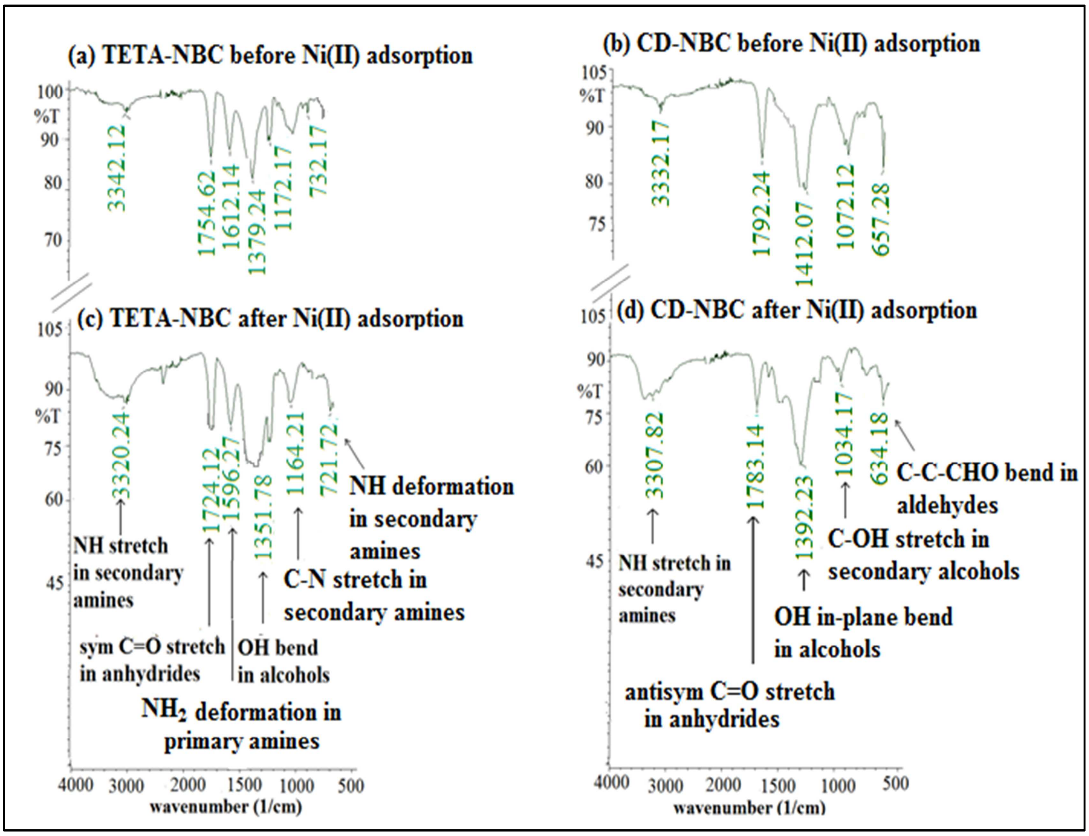

Fig 4: FT-IR spectra of TETA-NBC and CD-NBC before (a and b) after (c and d) Ni(II) adsorption

Instrumental analysis

Infrared spectra can yield valuable information regarding the functional groups involved before and after Ni(II) adsorption (Fig. 4(a-d)). As shown in Fig. 4(c), major peak stretches at 3320.24 cm^{-1}, 1724.12cm^{-1}, 1596.27cm^{-1}, 1351.78cm^{-1}, 1164.21 cm^{-1} and 721.72 cm^{-1} confirmed the involvement of amines (primary and secondary), anhydrides and alcohols in case of TETA-NBC whereas in case of CD-NBC major peak stretches at 3307.82 cm^{-1}, 1783.14 cm^{-1}, 1392.23 cm^{-1}, 1034.17 cm^{-1} and 634.18 cm^{-1} confirmed the involvement of secondary amines, anhydrides, alcohols and aldehydes (Fig. 4(d)). Moreover, a higher number of functional groups were found to be involved in case of TETA-NBC. The number of peak stretches and transmittance of amine functional group noted in

TETA-NBC was found to be higher as compared to CD-NBC owing to the higher availability of amine groups in case of TETA-NBC which validated TETA-NBC as potential adsorbent for the remediation of Ni(II) ions from aqueous solution.

The analysis of TETA-NBC and CD-NBC using scanning electron microscopy (SEM) was conducted to get further insight into the surface topology before and after Ni(II) adsorption (Fig. 5(a-d)). A high surface roughness and raised structure was noted in case of TETA-NBC (Fig.5(a)) when compared to CD-NBC (Fig. 5(b)) which could be possibly due to the addition of amine molecules and exposure of functional groups in the former case which enhanced the uptake of Ni(II). In case of CD-NBC (Fig.5(b)) a higher compaction was noted due to the higher interaction between the hydroxyl groups of CD-NBC and aldehyde moieties of glutaraldehyde which accounted for the surface smoothness and lower adsorption potential [36]. After Ni(II) adsorption, a more electron dense part (bright region) which was due to nickel adsorption was noted in case of TETA-NBC (Fig. 5(c)) when compared to that of CD-NBC (Fig.5(d)). Similar result was reported where Ni(II) ions were removed using sericite beads [37].

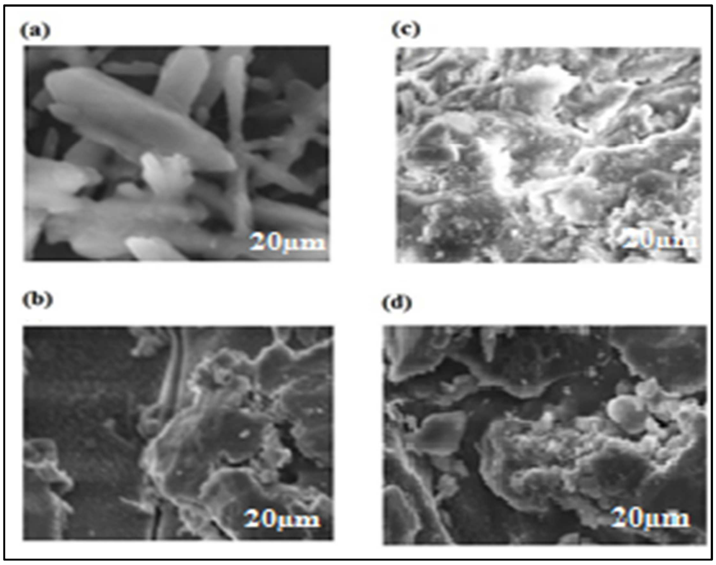

Fig 5: SEM analysis of TETA-NBC and CD-NBC before (a and b) after (c and d) Ni(II) adsorption

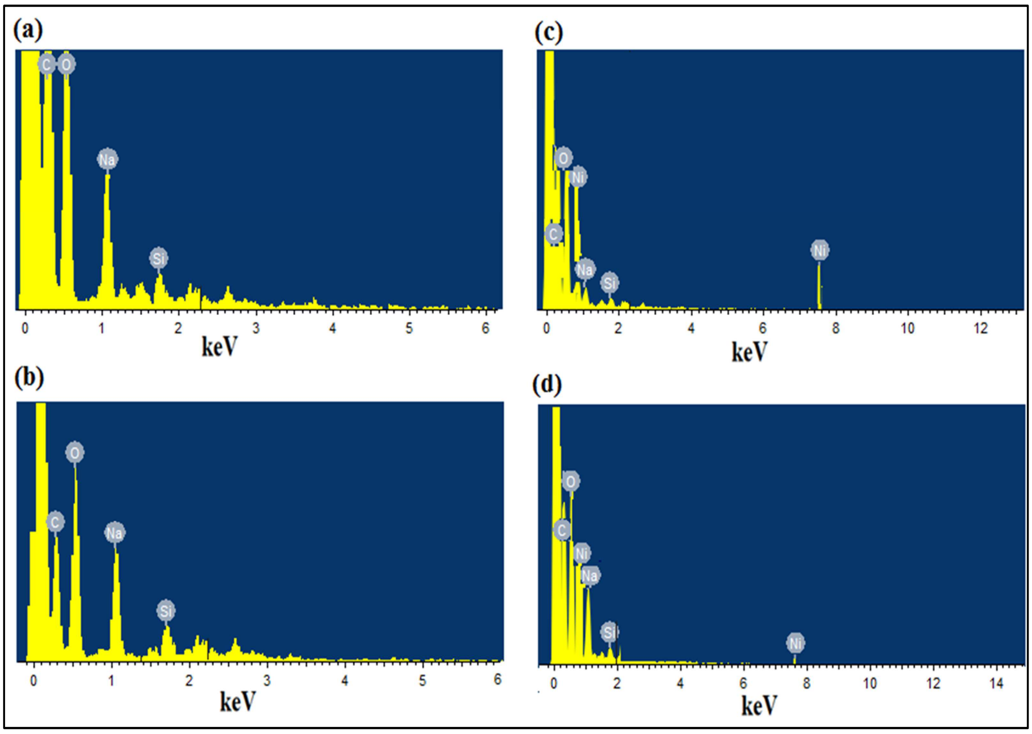

Fig 6: EDX spectra of TETA-NBC and CD-NBC before (a and b) after (c and d) Ni(II) adsorption

The elemental compositions of TETA-NBC and CD-NBC were analyzed using EDX (Fig. 6(a-d)). The EDX spectrum before Ni(II) adsorption (Fig. 6(a-b)) indicated the presence of C and O as natural species on the surface of the NBCs whereas the peaks of Na and Si confirmed the presence of clay in both TETA-NBC and CD-NBC. After Ni(II) adsorption an intense Ni peak was observed in case of TETA-NBC (Fig. 6(c)) as compared to CD-NBC (Fig. 6(d)). A significant decrease in the peaks of C, O, Na and Si was noted for both NBCs which validated their involvement in the adsorption process. Moreover, a higher decrease in C peak in case of TETA-NBC confirmed its higher uptake potential compared to CD-NBC.

CONCLUSION

In this study, we report the application of TETA-NBC and CD-NBC for the removal of Ni(II) ions from aqueous environments. Maximum Ni(II) removal (99.34%) was shown by TETA-NBC under optimized condition (pH: 6.0, time: 10h, temperature: 40°C, initial Ni(II) concentration: 400 mg/L, adsorbent dosage: 0.8 g/L). Equilibrium and kinetic studies were performed to study the mode and rate of adsorption. Equilibrium sorption data showed an excellent fit to Langmuir isotherm model, indicating a monolayer mode of Ni(II) adsorption onto the surface of both TETA-NBC and CD-NBC. The result of adsorption kinetic studies suggested a physical mode of adsorption via both intra-particle and film diffusion mode. Thermodynamic studies defined the adsorption process as endothermic in nature. Elucidation of mechanism was done using SEM, EDX and FT-IR analyses. Results suggested that in case of TETA-NBC, a higher Ni(II) uptake was noted due to enhanced surface roughness, less compaction and higher exposure of amine functional groups when compared to that of CD-NBC.

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