

Adsorptive removal of Ni and Cd by bentonite from aqueous system

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ABSTRACT

Bentonite clay mineral rich in montmorillonite was characterized and evaluated for removal of Ni and Cd from aqueous solution by batch adsorption study. The variables which affect metal sorption capacity such as adsorbent dose, pH and initial concentration of metals on the extent of adsorption were investigated. The experimental data were fitted with Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich adsorption isotherms. The Langmuir and Freundlich adsorption isotherms were fitted the sorption data better than other isotherms. The Langmuir maximum monolayer adsorption capacity of bentonite was found to be 13.95 mg g⁻¹ and 9.41 mg g⁻¹ for Ni (II) and Cd (II), respectively. The study revealed that bentonite could be potentially used for removal of Ni (II) and Cd (II) ions from effluents laden with heavy metals.

Key words: Bentonite, Heavy metal, Adsorption, Langmuir

Introduction

Pollution of water with toxic substances is of major concern for human health as well as for the environmental quality. Heavy metals are generated and discharged to the environment as wastes by several industries like power plants, waste incinerators, turbine production, battery manufacturing and assembly, and mining activities (Bhattacharya *et al.*, 2006; Chen *et al.*, 2009). The heavy metals are known to be highly toxic at very low concentrations and they can be distinguished from other toxic pollutants, since they undergo chemical transformations, are non-biodegradable, and have great environmental, economic, and public health impacts (Fu and Wang, 2011). In addition, heavy metal contamination in the

surface- and ground water environment prevents any beneficial use of the water bodies. Therefore, control of heavy metals in waste effluents before its disposal into the water bodies is essential. Conventional technologies in heavy metal removal include precipitation, ion exchange, reverse osmosis, and filtration. However, these methods have several disadvantages/limitations such as being expensive, generating secondary pollutants like sludge, and ineffective in treating effluents with low metal concentrations etc. Among the physico-chemical treatments, adsorption process is easy to operate and can treat waste effluents with high loadings and at very low concentrations. A number of studies have been carried out for the removal of heavy metals using natural materials like clay, zeolite biopolymers such

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as chitosan, cellulose and starch (Kuniawan *et al.*, 2006) from aqueous system with varying degree of success. Use of clay minerals to remove metals has been increasingly paid attention because of their mechanical stability, low cost, availability, high surface area, presence of metal chelating functional groups and negative charge on surface can be used as potential materials for improving the effluents (Fu and Wang, 2011) In this study bentonite was evaluated for their potential heavy metal removal from aqueous system as well as metal sorption capacity of a contaminated soil.

Materials and Methods

Instrumentation

FTIR is one of the most widely used tools for the detection of functional groups in pure compounds and mixtures and for compound comparison. Infrared (IR) study is related to the vibrational motion of atoms or molecules. In terms of frequency, the IR regions extend from 3×10^{12} Hz to 3×10^{14} Hz and in terms of wave number it extends from 100 cm^{-1} to 10^4 cm^{-1} . This study is mainly used for structure elucidation in organic and inorganic compounds. These compounds absorb electromagnetic energy in the infrared region of the spectrum. IR radiation does not have sufficient energy to cause the excitation of electrons. However, it causes atoms or group of atoms to vibrate faster about the bonds, which connect them. The compounds absorb energy from a particular region since the vibrations are quantized. The position of a particular absorption band is specified by a particular wave number. Infrared spectroscopy of the powdered samples was carried out by using the Bruker: ALPHA, FTIR/ ATR system (24 scans, resolution- 4 cm^{-1}). Clay samples were scanned in the region of $4000 - 400 \text{ cm}^{-1}$ using KBr pellets. All the spectra were recorded and analysed to know the type and nature of the functional group attachment.

Materials and reagents

All chemicals were of analytical grade purchased from SRL, India used in the experiment without further purification. Bentonite mineral was purchased from Minerals limited, New Delhi, India. Stock solutions of metals (Ni and Cd) containing 1000 mg L^{-1} metal ion was prepared by dissolving appropriate amount of AR grade sulphate [$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] salts of heavy metals separately in

double distilled water. The working standard solutions of metals were prepared from the stock solution by appropriate dilution using double distilled water.

Adsorption experiments

All the adsorption equilibrium experiments were conducted by batch method. A known volume (50 mL) of metal solutions of varying initial concentrations (0 to 50 ppm), in polypropylene bottle was shaken with a desired dose of adsorbent for a specified contact time in an end to end shaker. After the pre-determined adsorption time, solution was filtered through Whatman No.42 filter paper. The initial and equilibrium concentrations of metal in the aqueous solutions were analyzed by atomic adsorption spectroscopy (AAS). The amount of metal adsorbed (Q in mg g^{-1}) was determined as follows:

$$Q = [(C_0 - C_t) / m] V$$

where Q is the amount of metal ions adsorbed onto unit amount of the adsorbent (mg g^{-1}), C_0 and C_t are the initial and terminal concentrations of metal in solution (mg L^{-1}), V is the volume of solution (L) and m is the mass of the adsorbent (g), respectively. The percentage removal of metal ion was calculated by following equation:

$$\text{Removal (\%)} = [(C_0 - C_t) / C_0] 100$$

where C_0 and C_t are the initial and terminal concentrations of metal in solution (mg L^{-1})

The distribution coefficient of an adsorbent is defined as the ratio of the metal ion adsorbed to the amount in the liquid phase. The distribution coefficient was calculated according to the following equation:

$$\text{Distribution coefficient (K}_d, \text{ L/g)} = [(C_0 - C_t) / C_t] * V / m$$

where C_0 and C_t are the initial and terminal concentrations of metal in solution (mg L^{-1}), V is the volume of the solution (L) taken and m is the mass of adsorbent (g) taken.

Effect of adsorbent level: To examine the effect of adsorbent level on metal adsorption, 50 mL of 25 ppm metal solution with different amount of bentonite (0.01, 0.025, 0.05, 0.1, and 0.2 g) in polypropylene bottle was shaken for a specified contact time (4hrs) in an end to end shaker. After the pre-determined adsorption time, solution was filtered with Whatman No.42 filter paper. The initial and equilibrium concentrations of metal in the aqueous solutions were analyzed by the atomic adsorption spectrophotometer (AAS).

Effect of pH: To examine the effect of pH on metal adsorption, 50 mL of 25 ppm metal solution with different pH values (1, 2, 3, 4, 5, 6, 7 and 8) and 0.1 g of adsorbent in polypropylene bottle was shaken for a specified contact time in an end to end shaker. After the predetermined adsorption time, solution was filtered with Whatman No.42 filter paper. The initial and equilibrium concentrations of metal in the aqueous solutions were analyzed by the atomic absorption spectrophotometer (AAS).

Results and Discussion

Characterisation of bentonite

Figure 1 shows the FTIR spectra of the bentonite which shows.

Effect of adsorbent level

Amount of adsorbent is an important parameter which determines adsorption capacity. The dependence of metal adsorption on bentonite was studied by varying the amount of adsorbent from 0.01 to 0.2 g while keeping other parameters such as pH of the solution, concentration (25ppm), metal solution volume (50mL) and contact time (4 hrs) constant. The data (Figure 4 a and b) indicate that in all the cases percentage removal of metal increased from 35% to 88%, and 30% to 67%, for Ni (II) and Cd (II), respec-

tively. The increase in percentage of removal as dosage was increased due to the increase in surface area of adsorbent. A higher adsorbent dosage also reflects a greater number of available adsorption sites (Vijayaraghavan *et al.*, 2011) therefore more metal ions were able to be adsorbed. However reduction in adsorption capacity of bentonite with increase in dose of adsorbent was observed for both the metals. As the dosage increased, the ratio of number of adsorption sites to the number of metal ions would increase because fixed amount of metal ions results in more number of unadsorbed adsorption sites. At higher adsorbent dose particle aggregation may decrease the total surface area of the adsorbent and leads to lower efficiency of adsorbent.

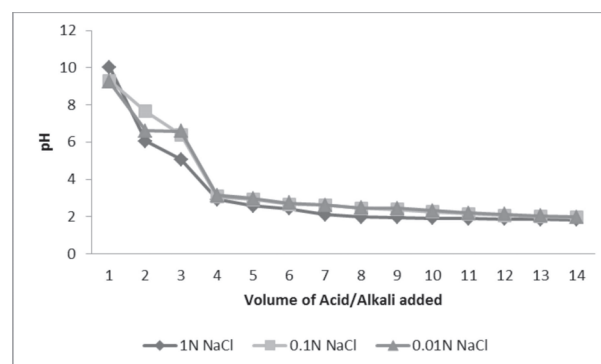


Fig. 2. Potentiometric titration curve of bentonite

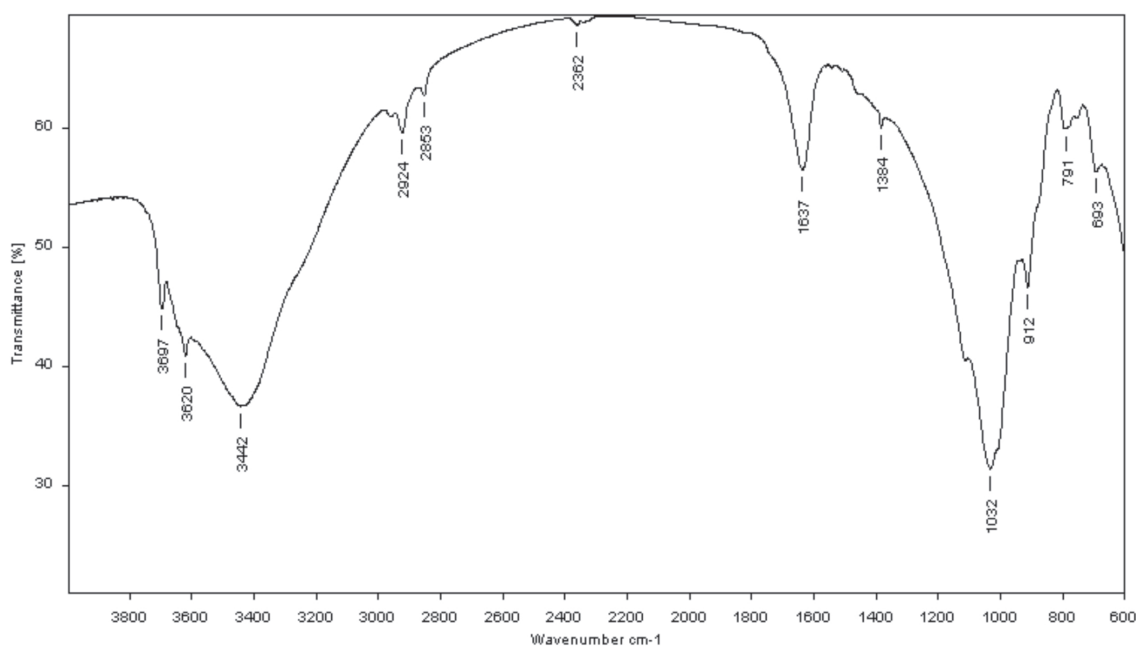


Fig. 1. FTIR spectrograph of bentonite

Effect of pH

The effect of pH on adsorption of metal ions by bentonite was studied with different pH values at same level of metal concentration (25 ppm) and adsorbent (0.1g). The pH of the solution strongly affects the adsorption capacity of bentonite. Figure 5 (a) and (b) show that adsorption of metals increases with increasing pH of the solution. The results indicate that maximum adsorption of Ni (II) and Cd (II) occurs at pH 7 respectively. There is no general agreement on a simple mechanism responsible for this behaviour, but strong adsorption of metal hydroxide complexes (Forbes *et al.*, 1974), hydrolysis of Al on exchange sites (Cavallaro and McBride, 1980), Lower adsorption of metals at acidic pH is attributed to higher concentration of H^+ and hydronium (H_3O^+) ions and their competition with metal ions for adsorption sites (Newton *et al.*, 1976) and acid-catalysed dissolution of reactive oxide sites (Elliot and Huang, 1979) may be involved. The diminution of the adsorption rate of metals by bentonite with a decrease-

ing of pH of solution is in agreement with the theory that considers that a pH decrease involves a diminution of the cation exchange capacity (CEC) of the sorbent (bentonite), and in consequence a metal removal diminution. At pH above isoelectric point the surface becomes negatively charged and the functional groups such as hydroxyl, silanol and aluminol attract metal cation there by resulting in electrostatic interaction. At higher pH due to reduced inhibitory effect of H^+ metal adsorption increases. Ni (II) and Cd(II) get precipitated at pH above 7 respectively resulted in lower adsorption.

Effect of initial metal concentration

The effect of initial metal concentration on adsorption of metal ions was studied with varying metal concentration at same level of pH, adsorbent (0.1g) and contact time (4 hrs). Figures 6a and b show the effect of initial metal concentration on percentage removal and sorption capacity per unit amount of adsorbent. Percentage removal of metal decreased with increase in initial concentration and the reverse

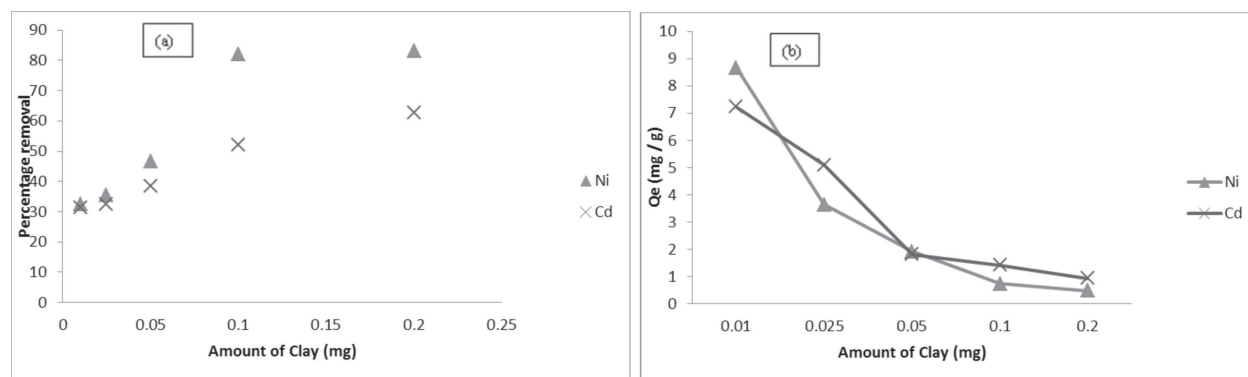


Fig. 3. Effect of adsorbent dose on percentage removal (a) and amount of metal adsorbed per unit amount of adsorbent (b)

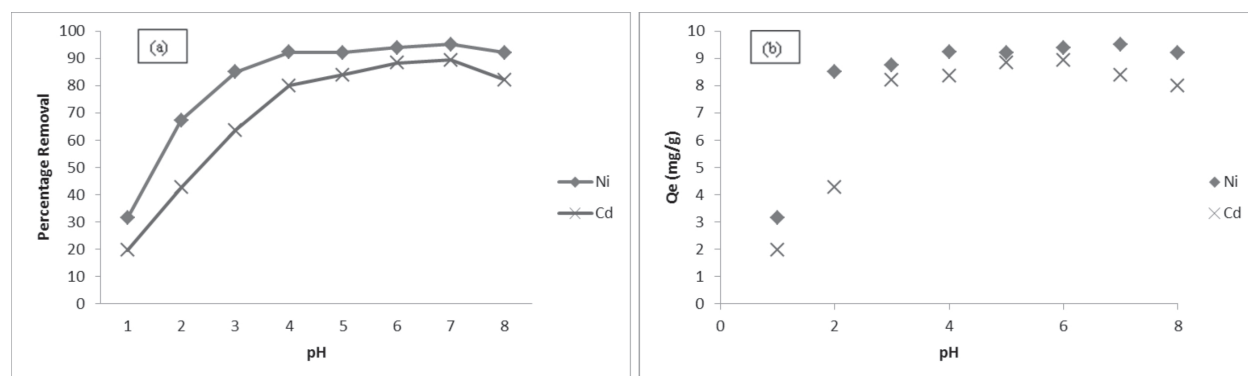


Fig. 4. Effect of pH on percentage removal (a) and adsorption capacity (mg/g) of bentonite (b)

trend observed in case of sorption capacity per unit amount of adsorbent. At low metal concentration, the adsorption capacity significantly increased with increasing metal concentration because of increased level of metal ions in the solution enhanced the interactions between metal ions and the active sites of the adsorbent. The initial concentration of metal ions act as an important driving force to overcome all mass transfer resistance of metal ions between the solid and solution phase.

Adsorption isotherms

An adsorption isotherm reveals the mathematical relationship between the adsorption capacity and equilibrium concentration of an adsorbent at a constant temperature. The Langmuir and Freundlich models are often used to describe the adsorption isotherm. To obtain adsorption isotherm initial concentration varied between 5-100 ppm while keeping pH, adsorbent dose (0.1g) and contact time (24hr) constant. The adsorption data were analysed with the Langmuir and Freundlich isotherm models.

The Langmuir equation suggests that the sorption occurs at the solid surface that is made up of elementary sites, each of which can adsorb one sorbate molecule, *i.e.* monolayer sorption. It was also assumed that every sorption site is equivalent and the ability of the sorbate to get bound there is independent of whether or not the neighbouring sites are occupied [38]. The Langmuir equation is given as follows:

$$Q_e = (Q^0 b C_e) / (1 + b C_e)$$

The linear version of Langmuir equation is:

$$C_e / q_e = 1/Q^0 b + C_e/Q^0 + 1$$

where Q^0 is the maximum adsorption at mono-

layer (mg g^{-1}), C_e is the equilibrium concentration of metal (mg L^{-1}), q_e is the amount of metal adsorbed per unit weight of composite, b is the Langmuir constant related to affinity of binding site (L mg^{-1}) and is a measure of energy of adsorption. A linearized plot of C_e / q_e against C_e gives Q^0 and K_L . In general for good adsorbents, high value of Q^0 and low values of b are required. The essential characteristics of Langmuir dimensionless constant separation factor or equilibrium factor R_L that is used to predict whether the adsorption process is unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The product of Q^0 and K_L has been used by many authors to estimate Gibbs free energy by the following formula:

$$\Delta G = -RT \ln K$$

where K represents the product of Q^0 and K_L . ΔG may be used to address the spontaneity and feasibility of the process.

Based on the Langmuir isotherms, (Figure 6a) the Langmuir parameters and correlation coefficients (Table 1) of metal adsorption were calculated for the studied metals namely nickel and lead. Langmuir constant Q^0 , represent the maximum monolayer adsorption capacity of the bentonite. The values are 10.8 mg g^{-1} and 9.4 mg g^{-1} for Cd (II) and Ni (II), respectively. The Langmuir isotherm described the sorption data of Cd and Ni on bentonite and based on the maximum adsorption capacity values the sequence of metal sorption was found to be Ni (II) > Cd (II). The sequence of Q^0 was consistent with the first hydrolysis constants (K_h) of the metals studied *i.e.*, Ni ($10^{-9.9}$) and Cd ($10^{-10.1}$). Metals with larger K_h (lower $\text{p}K_h$ values) form surface hydroxo species within given pH range and are chemisorbed to the

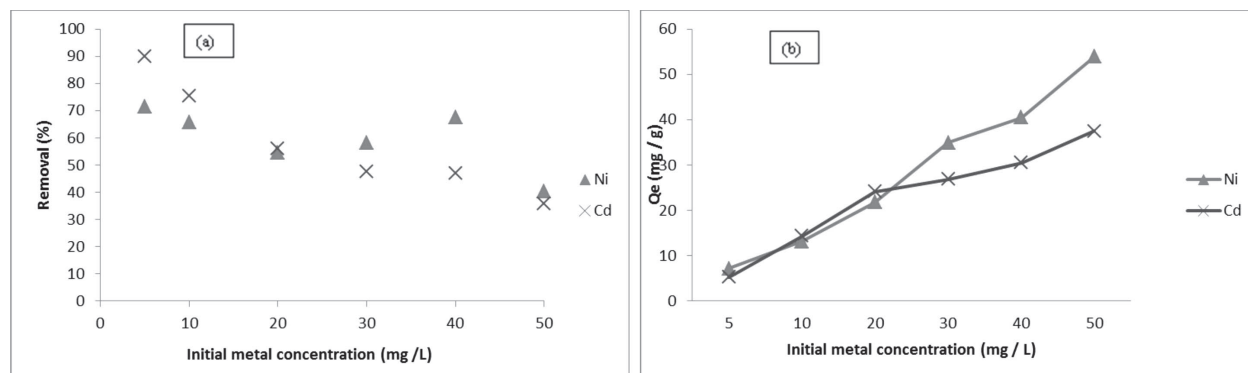


Fig. 5. Effect of initial concentration on metal adsorption capacity (a) and percentage removal of metals (b) by bentonite

surface to a greater extent. The Langmuir dimensionless factor (R_L) values (Table 2) varied between 0.8832-0.1042 for cadmium and 0.8489-0.1011 for nickel. The R_L values at concentrations of 5-50 ppm are in the range of $0 < R_L < 1$, which indicate that the adsorption of Ni and Cd ions onto bentonite is favourable and it implies that bentonite is an opt adsorbent for the removal of Cd (II) and Ni (II). The distribution coefficient (K_d) is a useful index for comparing the sorptive capacities of materials for a particular ion under the same experimental conditions. Therefore, a further analysis of the obtained data based on the distribution coefficients was done. The distribution coefficient (K_d) has been calculated over all the initial concentrations of heavy metals

(Figure 7). It is defined as the ratio of the metal concentration in the solid phase to that in the equilibrium solution after a specified reaction time. A high K_d value indicates a higher metal retention by the adsorbent through sorption and chemical reactions. However, a low K_d value indicates a high amount of the metal remains in the solution. Over all initial concentrations of heavy metals, the highest K_d values were found for Cu and followed by those of Zn that showed intermediate K_d values (Figure 7). However, low K_d values were pronounced for Cd and Ni. This implies that Cu and Zn are the most strongly sorbed metals by the composite, whereas Cd and Ni are the least sorbed ones. The results also indicated that the K_d value decreased with increasing the initial metal concentration (Figure 7). This indicates that changes occur in the nature of the sites that are involved in the sorption process, depending upon the metal concentration. The higher K_d value that was obtained in the experiment with lower metal concentrations is associated with the sorption sites of high selectivity, which have relatively strong

Table 1. Isotherm constants for metal sorption on bentonite and correlation coefficients

Parameters	Ni	Cd
Langmuir Isotherm		
Qm (mg/g)	10.8	9.4
K_L (L/g)	0.42	0.88
R^2	0.99	0.97
Freundlich isotherm		
K_f (mg/g) (L/g) ^{1/n}	4.60	3.68
1/n	0.23	0.29
R^2	0.83	0.98
Tempkin Isotherm		
B (mg/g)	11.7	8.4
K_T (L/g)	1.55	1.31
b_T (J/mol)	216	300
R^2	0.91	0.85
Dubinin-Radushkevich isotherm		
q_{DR} (mg/g)	0.012	0.53
K_d (mmol ² /kJ ²)	0.82	0.95
E (kJ/mol)	1.22	1.06
R^2	0.93	0.90

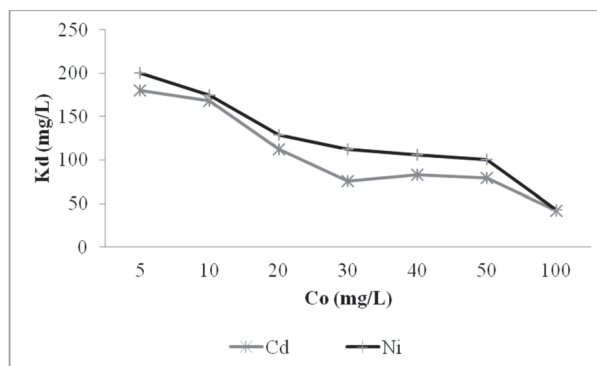


Fig. 7. Distribution coefficients of Nickel and Cadmium

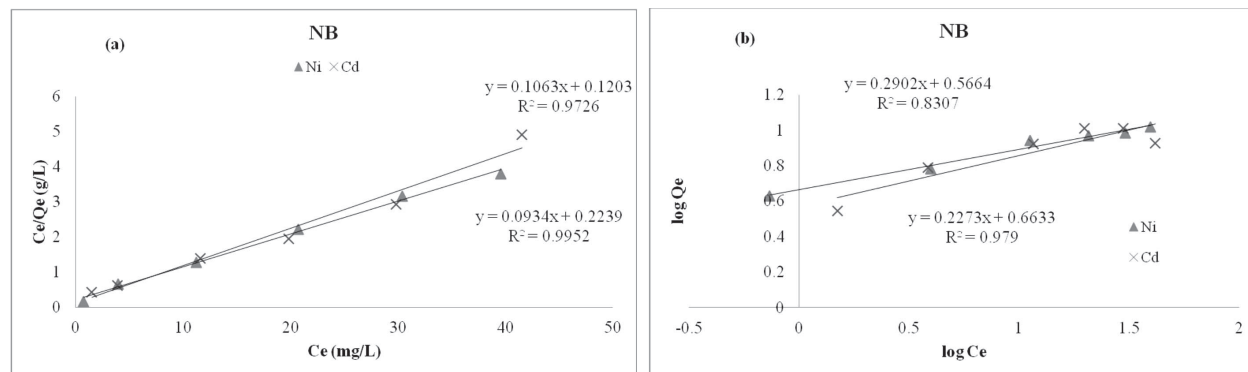


Fig. 6. Langmuir (a) and Freundlich (b) adsorption isotherms of Nickel and Cadmium

Table 2. Langmuir isotherm dimensionless separation factor (R_L) values

Initial metal concentration (mg/L)	R_L	
	Ni	Cd
5	0.8260	0.8137
10	0.5123	0.5074
20	0.3876	0.3435
30	0.2091	0.2050
40	0.1370	0.1324
50	0.1201	0.1206

bonding energies. Otherwise, heavy metal sorption becomes unspecific at higher metal concentrations, when the specific bonding sites become increasingly occupied, resulting in lower K_d values. The sorption of heavy metals by chitosan biopolymer bentonite composite is favourable and spontaneous one because of the negative value of ΔG (Table 1).

The Freundlich isotherm is an empirical equation and is one of the most widely used isotherms for the description of multi-site adsorption where the adsorbent surface is heterogeneous in nature. Mathematically, it is expressed as

$$q_e = K_f \times C^{1/n}$$

where q_e is the amount of metal ion adsorbed (mg g^{-1}) onto chitosan biopolymer bentonite composite. The parameters of Freundlich isotherm, K_f and n indicating the sorption capacity and intensity, respectively. When $1/n$ reaches its maximum value of 1, K_f can be considered as partitioning coefficient showing the ratio of metal sorbed to solid phase to that remains in the bathing solution at equilibrium. Linear plots of $\log q_e$ versus $\log C_e$ ($\log q_e = \log K_f + 1/n \log C_e$) for the different initial metal ion concentrations gives K_f and n . The Freundlich constant n value indicate the favourability of the adsorption process with values < 1 for poor adsorption, 1-2 for moderately good and 2-10 represent the beneficial adsorption. The Freundlich parameters calculated from the Freundlich isotherm (Figure 6b) along with the correlation coefficient are given in Table 1. Cu(II) has the highest K_f and n values over Zn(II), Cd(II) and Ni(II). Cu (II) with the highest n value means it has highest affinity towards the functional groups of the composite and stronger bond results in higher K_f . According to Freundlich adsorption theory, the n values between 1 and 10 indicate beneficial adsorption, and in this study the n values are more than unity for all the four metals which demonstrates the beneficial adsorption.

Conclusion

The FTIR analysis confirmed the functional groups and potentiometric titration showed the zeta potential of bentonite clay mineral. The effect of adsorbent level, initial metal concentration and pH on metal sorption capacity of bentonite showed maximum sorption of Ni and Cd at pH 7 and the percentage removal of metal decreased with increase in initial concentration and the reverse trend observed in case of sorption capacity per unit amount of adsorbent. Amongst the adsorption isotherms, Langmuir equation fitted well and the study demonstrated the usefulness of bentonite in removal of metals from aqueous solution by adsorption mechanism.

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