



ADSORPTION OF ARSENIC(V) ONTO METAL LOADED CELLULOSE NANOCOMPOSITE BEAD (MCNB)-ISOTHERM AND THERMODYNAMIC STUDY

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Cellulose nanocomposite bead modified with metal (MCNB) such as Ce, Al and Fe is synthesized for selective adsorption of arsenate anions As(V) from drinking water in batch system. The adsorbent was characterized by FTIR, FESEM, EDS and EPR studies. In the present report arsenic(V) adsorption performance on cerium modified cellulose bead was described. The maximum adsorption of As(V) is near about 100 percent up to an initial arsenic load of 5.0 mg L⁻¹ at the acidic pH of 3.0 and the equilibrium is reached in 5 h. The much higher adsorption extent and quick equilibrium time compared to the other reported adsorbents makes the present adsorbent as efficient one. Among the three adsorption isotherm models used, Langmuir model fitted the experimental data best. The adsorption is found to be exothermic, spontaneous and random in nature. The process was applied for removal of arsenic from some real sample.

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Various treatment technologies have been used to remove arsenic from water such as oxidation,⁵ coagulation,⁶ ion exchange,⁷ chemical precipitation,⁸ membrane separation,⁹ etc. However, adsorption is recognized as an effective technique due to availability of wide range of adsorbents including natural and synthetic materials. The high concentration efficiency, simple operation, and environmental friendly behavior¹⁰ of certain adsorbents make the process quite popular. Cellulose, the most widely available and renewable biopolymer in nature, is a very promising raw material available at low cost for the preparation of various functional materials. Due to the presence of hydroxyl groups, cellulose may undergo surface modification.^{10,11} Cellulose beads show good adsorption ability due to their unique hydrophilic and porous nature as well as high surface area. Beads made from cellulose and its derivative are commonly used as ion exchangers, packing materials for chromatography, adsorbents for heavy metal ions, and proteins, cosmetic additives, and carriers for immobilization of biocatalysts.¹²⁻¹⁴ However, studies on cellulose beads as arsenic scavenger are still scarce. Adsorbents modified with metals such as Fe,^{15,16} Ce,¹⁷ Ti,^{18,19} Al,²⁰ La,^{21,22} etc are found to have potential ability to absorb arsenic from water under optimized condition. In the present investigation cerium loaded nanocomposite cellulose bead (CCNB) for As(V) adsorption is reported as a representative of the metal loaded nanocomposite cellulose bead.

Introduction

Arsenic (As) contamination in ground water is one of the most critical environmental problems today. Arsenic (atomic number 33) is ubiquitous and ranks 20th in natural abundance, comprising about 0.00005 % of the earth's crust, 14th in the seawater, and 12th in the human body.¹ Arsenic, due to its toxic and carcinogenic effect, has been recorded by the World Health Organization as a first priority pollutant.^{2,3} Acute and chronic arsenic poisoning via drinking water has been reported in many countries, especially Argentina, Bangladesh, India, Mexico, Mongolia, Thailand, and Taiwan, as a result of in groundwater⁴ arsenic load at levels from 100 to over 2000 µg L⁻¹.

Millions of people worldwide are exposed to naturally occurring arsenic contaminated groundwater, which they use as their sole source of drinking water. Increased use of groundwater as a source for drinking water has caused serious health problems such as neurological, dermatological, gastrointestinal, cardiac, and renal diseases. Factors such as anthropogenic activities, biological actions, and geochemical reactions accelerate arsenic mobilization into groundwater.¹ Arsenic compounds are stable in the environment, have a tendency to bioaccumulate in the food chain, and can undergo biotransformation with an increase in toxicity. It is necessary to control the arsenic concentration in environmental samples, industrial wastes, biological materials, and foods.

The synthesized bead was characterized by Fourier transformed infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS) and electron paramagnetic resonance (EPR) study. The feasibility of equilibrium adsorption was interpreted by adsorption isotherms such as Langmuir, Freundlich, and Temkin model as well as the thermodynamic parameters such as change in free energy, enthalpy, and entropy.

Experimental

Materials

All the chemicals used are of analytical grade (Merck, India). The cellulose powder used was procured from Loba Chemie, Mumbai, India

Preparation of CCNB

Cerium loaded cellulose nanocomposite bead was synthesized by the method described elsewhere²³ following sol gel techniques.

1 g of cellulose is esterified with carbon disulfide with shaking in alkaline medium and stirred for 3 h.²⁴ The sol was allowed for ageing (syneresis) at room temperature for 72 h and the gel probably formed by condensation of the sol, was purged drop by drop into de-aerated methanol through a needle. A faint red colored beads initially formed were filtered and immediately washed several times with double distilled water. The cellulose beads appeared as snow white, were stored under de-ionized water.

The cellulose nanocomposite beads were next poured into a solution of 0.10 M cerium ammonium nitrate at pH 1.6 and shaken at a speed of 100 spm at room temperature for 2 h. A faint orange yellow colored cerium loaded cellulose nanocomposite bead, (CCNB) was formed, washed with distilled water, and stored under de-ionized water.

Characterization of CCNB

Field emission scanning electron microscope (FESEM) with a JEOL, JSM 6700F microscope was used to study surface morphology and energy dispersive spectroscopy (EDS, model FEI QUANTA FEG 250) was used for element detection. Electron paramagnetic resonance (EPR) study to identify the binding pattern of cerium in the bead was recorded in a Varian X-band EPR spectrometer (Model E-109). The Fourier transformed infrared (FTIR) spectral study was recorded in a Perkin Elmer L120-000A spectrophotometer.

Batch adsorption study

Batch adsorption experiment was performed using As(V) solution of known concentration, shaken with a specific amount of CCNB, and agitated at a constant shaking rate of 120 spm in a temperature controlled shaker. The initial solution pH was adjusted using 0.1 M HCl/NaOH. The As(V) concentration in solution was determined using atomic absorption spectroscopy (AAS, Varian AA240 model). Adsorption efficiency (ϕ , in %), expressed as percent adsorption, was calculated using the following equation:

$$\phi = 100 \frac{C_0 - C_e}{C_0} \quad (1)$$

where,

C_0 and C_e are the initial and equilibrium As(V) concentration (mg L^{-1}), respectively in solution.

Result discussion

Characterization of CCNB

Physicochemical parameters such as bulk and material density were found to be 0.902 and 0.410 g cm^{-3} respectively. The degree of swelling was found to be 22 while the water content and porosity were found to be 95.120 and 89 % respectively.

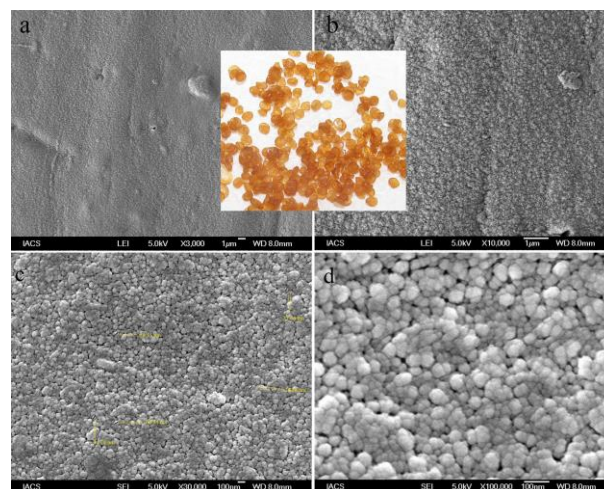


Figure 1. FESEM at different magnification and physical image (inset)

The surface structure of CCNB, as revealed from FESEM analysis, indicates the spherical nature of the bead with an average size in the range 28 to 61 nm (Fig. 1). The EDS shows peaks corresponding to the presence of 'C', 'O' and 'Ce' in the CCNB (Fig. 2).

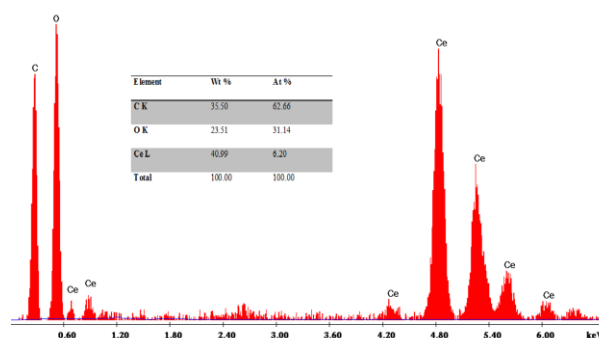


Figure 2. EDS of CCNB with table of weight percentage of element

The EPR study conducted at room temperature (303 K) and lower temperature (77 K) shows similar signals having characteristics g values attributed to $g_e=2.03$, $g_{\perp}=1.98$, $g_{\parallel}=1.93$, ($g_e > g_{\perp} > g_{\parallel}$)²³ corresponding to Ce^{3+} . The FTIR spectral analysis of CCNB showing the characteristic bands of cellulose moiety with characteristic linkages²⁵⁻²⁷ is presented in Table 1.

Table 1. FTIR spectral analysis of CCNB

Position, cm^{-1}	Assignment
3402	O–H stretching
2918	C–H stretching
1642	molecular water bending
1424	C–O–H and C–C–H deformations
1375–1317	C–H flexure (symmetric)
1161, 1060	C–O stretching
898	C–H bending (β -anomeric link of cellulose)
769	C–C stretching
535	Ce–O linkage

Effect of pH on As(V) adsorption

The effect of pH on As(V) adsorption by the CCNB is shown in Fig. 3 for the pH ranging between 2 and 12. It is observed that maximum adsorption of As(V) occurs at pH 3.0. pH dependent adsorption is significantly due to the specific arsenic species and the adsorbent surface charge. Speciation study indicates that the dominant species of arsenate are H_3AsO_4 (pH < 2), $H_2AsO_4^-$ (pH = 2–6.1), $HAsO_4^{2-}$ (pH = 6.1–11.5), and AsO_4^{3-} (pH > 11.5). It is probable that $H_2AsO_4^-$ is the most suitable species of arsenic for adsorption on CCNB.

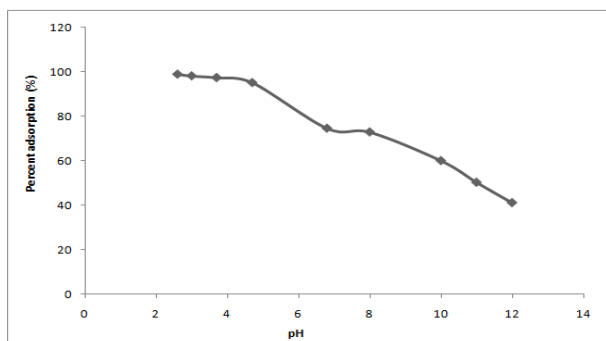


Figure 3. Effect of pH on As(V) adsorption

Effect of contact time on As(V) adsorption

Fig. 4 illustrates the effect of time on the percent adsorption as well as the attainment of equilibrium. It is found that with increase of time the percent adsorption corresponding to each concentration of As(V) increases. After a certain time it reaches a maxima forming a plateau. The time corresponding to maximum adsorption is known as the equilibrium time. It is observed that equilibrium is reached at 5 h for all the concentrations studied.

Effect of initial concentration on As(V) adsorption

The decrease in the percentage of As(V) adsorbed due to the increase in initial As(V) concentration at fixed adsorbent dosage is presented in Fig. 5. The increase in arsenic

adsorption capacity with the decrease in initial concentration was due to the availability of more adsorption sites. However, as the initial arsenic concentration increases, the ratio of the number of arsenic ions to the available active sites on the adsorbent becomes high and the arsenic ions are difficult to get adsorbed, leading to a decrease in the removal percentage.

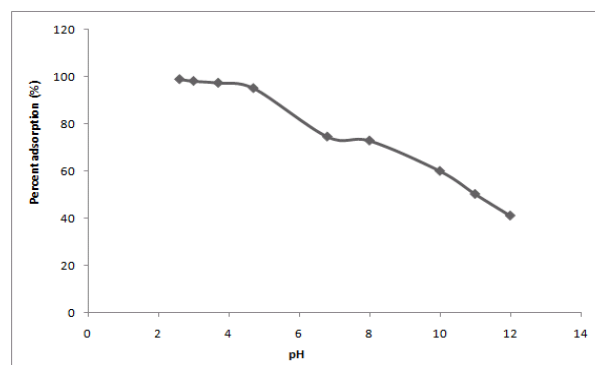


Figure 3. Effect of pH on As(V) adsorption

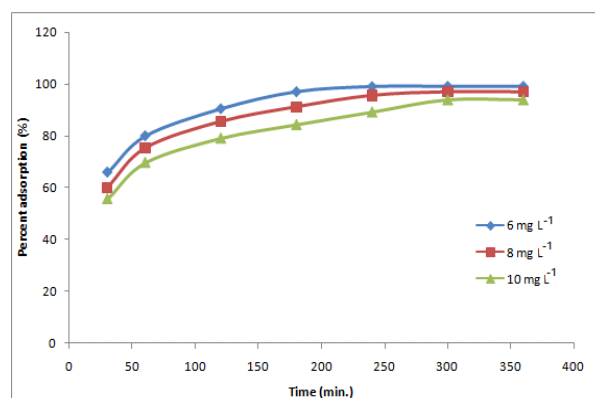


Figure 4. Effect of contact time on As(V) adsorption

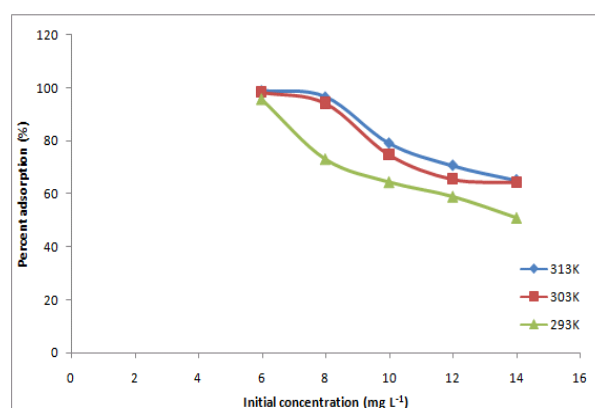


Figure 5. Effect of initial concentration on As(V) adsorption

Effect of adsorbent dose on As(V) adsorption

Fig. 6 showed that the increased adsorbent dose led to an increase in As(V) removal. The increase in percent adsorption with adsorbent dosage can be attributed to the increased adsorbent surface active sites.

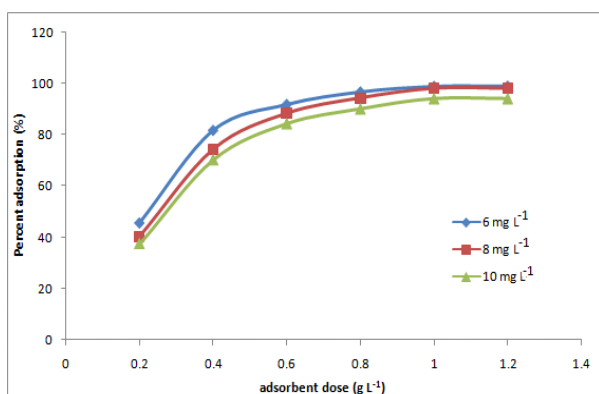


Figure 6. Effect of adsorbent dose on As(V) adsorption

Adsorption isotherm

In an aim to describe the equilibrium adsorption for As(V) ions from aqueous solution on CCNB, three most popular isotherm models viz. Langmuir, Freundlich, and Temkin are tested.

The Langmuir isotherm, (Fig. 7a) applicable for the monolayer adsorption²⁸ is expressed in its linear form as,

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{1}{Q}C_e \quad (2)$$

where,

Q (mg g^{-1}) and b (L mg^{-1}) are Langmuir isotherm constants signifying the adsorption capacity and the energy of adsorption respectively.

The Freundlich isotherm, (Fig. 7b) assuming an exponentially decaying adsorption site energy distribution and applicable to non-ideal adsorption on heterogeneous surfaces showing multi-layer adsorption,²⁹ is expressed by the following linear equation:

$$\ln q_e = \ln K_F + \frac{1}{nF} \ln C_e \quad (3)$$

where,

K_F is the constant indicative of the relative adsorption capacity of the adsorbent (mg g^{-1}), and

$1/n_F$ is the constant indicative of the intensity of the adsorption.

The Temkin isotherm,³⁰ (Fig. 7c) that considers solute/adsorbent interactions based on decaying heat of adsorption of the solute linearly with adsorbent surface coverage, is represented in linear form as,

$$q_e = \frac{RT}{b_{TM}} \ln k_{TM} + \frac{RT}{b_{TM}} \ln C_e \quad (4)$$

where,

k_{TM} is the isotherm constant and

b_{TM} is related to heat of adsorption.

The adsorption equilibrium data for As(V) adsorption at three different temperatures were determined and fitted to the above three isotherm equations. The quality of data fit was judged from the R^2 values. High R^2 value describes the most preferred situation. From Table 2 it is found that both the Q and b values increase with increase of temperature. This indicates that adsorption (Q) capacity increases with temperature. It is also supported by the fact that with higher temperature percent adsorption increase for each initial concentration of arsenic (Fig. 5). Among the three different isotherm models R^2 value corresponding to Langmuir is of higher magnitude than the Freundlich and Temkin model. Thus, Langmuir isotherm model most suitably describe the As(V) adsorption on CCNB.

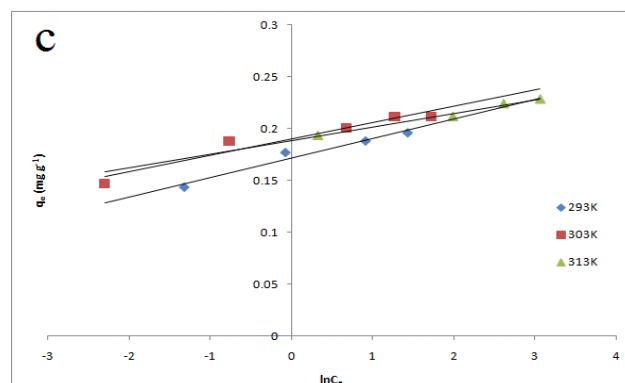
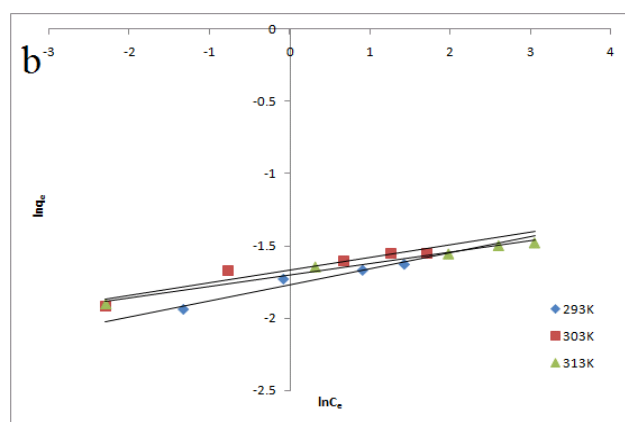
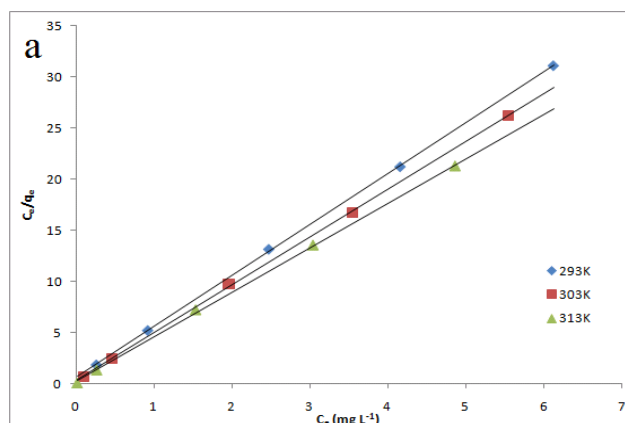


Figure 7. Isotherm data plots at different temperatures (a) Langmuir (b) Freundlich (c) Temkin

The applicability of Langmuir isotherm model was further tested by evaluating sf , the separation factor,³¹ a dimensionless quantity as expressed by

$$sf = \frac{1}{1 + bC_0} \quad (5)$$

where,

b is the Langmuir constant and

C_0 is the initial concentration of As(V).

The parameter ' sf ' indicates the nature of the isotherm as it is given in Table 3.

Table 2. Isotherm parameters

Langmuir isotherm	T , (K)	Q , (mg g ⁻¹)	b , (L mg ⁻¹)	R^2
	293	0.200	8.005	0.999
	303	0.214	14.590	0.999
	313	0.229	17.497	0.999
Freundlich Isotherm	T , (K)	K_F , mg g ⁻¹ (L mg ⁻¹) ^{1/n}	$1/n_F$	R^2
	293	0.170	0.111	0.945
	303	0.188	0.087	0.915
	313	0.182	0.078	0.985
Temkin isotherm	T , (K)	K_{TM} , (L mg ⁻¹)	b_{TM} , (kJ mol ⁻¹)	R^2
	293	1.330 x 10 ⁴	135.330	0.960
	303	3.148 x 10 ⁵	167.942	0.936
	313	1.901 x 10 ⁶	200.000	0.986

Table 3. Feasibility and nature of isotherm study

sf	Nature
$sf > 1$	Unfavorable
$sf = 1$	Linear
$0 < sf < 1$	Favorable
$sf = 0$	Irreversible

The sf value at each temperature corresponding to each concentration of As(V) is calculated (Table 4).

Table 4. Temperature dependent separation factor

T (K)	Sf , C_0 (mg L ⁻¹)		
	6.0	8.0	10.0
293	0.020	0.015	0.012
303	0.011	0.008	0.006
313	0.009	0.007	0.005

It is found that the sf values lie within 0.012 to 0.020 at 293 K, 0.006 to 0.011 at 303 K and 0.005 to 0.009 at 313 K. As all values lie between 0 to 1, the adsorption of As(V) on CCNB indicates a favorable case of adsorption.

Thermodynamic study

The knowledge of thermodynamic parameters is of fundamental importance to test the spontaneous occurrence of a given process as well as the feasibility of operation at a given temperature. Thermodynamic parameters associated with the adsorption process, viz., standard free energy change (ΔG^0), standard enthalpy change (ΔH^0), and standard entropy change (ΔS^0) were calculated using the following Eqs. 6 and 7.

$$\Delta G^0 = -RT \ln K_c \quad (6)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (7)$$

where,

T is the absolute temperature (K) and

R is the gas universal constant.

The equilibrium constant K_c for the adsorption was evaluated from the slope and intercept of the Langmuir plot³² (Fig. 7a).

The magnitude and sign of ΔG^0 depends on the value of K_c . When the rates of the adsorption and desorption processes are equal in magnitude, K_c becomes unity and $\Delta G^0 = 0$. The value of ΔG^0 is negative for $K_c > 1$ and positive for $K_c < 1$. If adsorption occurs spontaneously, the rate of adsorption being higher than desorption, ΔG^0 will always be a negative quantity.³³ Spontaneity of the adsorption process is also affected by the thermodynamic parameters ΔH^0 , and ΔS^0 .

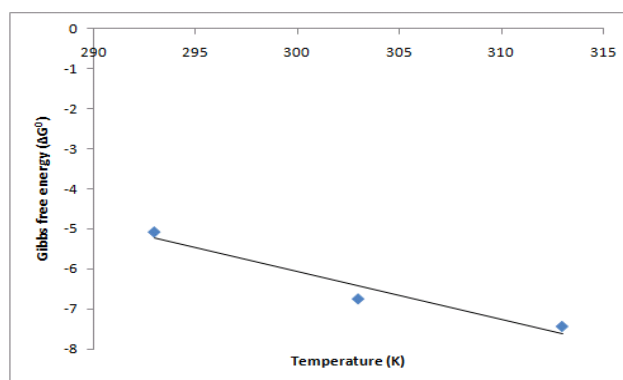


Figure 8. Plot of ΔG^0 versus temperature, T

A plot of ΔG^0 versus temperature, T , will be linear following equation (7) and the values of ΔH^0 , and ΔS^0 are determined from the slope and intercept of the plot Fig. 8. The values of K_c , ΔG^0 , ΔH^0 , and ΔS^0 are presented in Table 5.

Table 5. Thermodynamic parameters

T , (K)	K_c	ΔG^0 , (kJ mol ⁻¹)	ΔH^0 , (kJ mol ⁻¹)	ΔS^0 , (kJ mol ⁻¹ K ⁻¹)
293	8.005	-5.06705	29.63	0.119
303	14.59	-6.75215		
313	17.49	-7.44677		

Application

The efficiency of the present adsorbent is tested with the spiked samples. The results are shown in Table 6.

Table 6. Efficiency study with spiked sample

Sl. no.	As(V) concentration, (mg L ⁻¹)			Adsorption, (%)
	Mean	Spiked	Found	
1	0.5	0.0	0.51 ± 0.02	100
2	0.5	2.5	2.99 ± 0.02	100
3	0.5	5.0	5.44 ± 0.03	99
4	0.5	7.5	7.76 ± 0.04	97
5	0.5	10.0	8.56 ± 0.04	84

The applicability of the present method was judged with the field sample. The water sample was collected from some arsenic affected area of Deganga, North 24 Paragana, West Bengal, India. The composition of the field sample was presented in Table 7.

Table 7. Physicochemical parameters of the studied field sample

Parameter	Load, (mg L ⁻¹)
Hardness	142
pH	6.7
SO ₄ ²⁻	5.0
NO ₃ ⁻	Nil
Ca ²⁺	22.0
Mg ²⁺	5.0
Na ⁺	17.0
Iron	5.3
Arsenic	0.227

The load of the arsenic after treatment with CCNB was found to reach below the detection limit.

Conclusion

Metal loaded cellulose nanocomposite bead is found to be effective for adsorptive removal of arsenic from water. The process is dependent significantly on the pH of the solution. At acidic pH range quantitative adsorption occurs. The process is found to follow the Langmuir isotherm than the Freundlich and Temkin model. The process is thermodynamically feasible as shown by negative free energy change and positive entropy change. The process is effective for removing arsenic from real sample.

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