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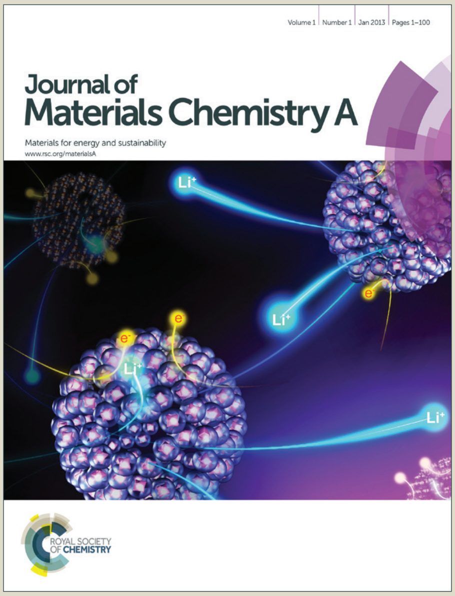

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Electrospun Chitosan-Polyvinyl alcohol composite nanofibers loaded with Cerium for efficient removal of Arsenic from contaminated water

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Abstract

Contamination of water due to arsenic has been extensively reported all over the world. It has led to massive epidemics of arsenic poisoning. To solve this problem, an urgent need is being felt to develop efficient techniques to remove arsenic from contaminated water. In this context, cerium (Ce) loaded Chitosan (CHT)-polyvinyl alcohol (PVA) composite (Ce-CHT/PVA) nanofibers were developed by electrospinning technique which has been employed for removing As (III). The Ce-CHT/PVA composites nanofibers efficiently adsorb As (III) and purify water below the prescribed limit of WHO/EPA. The As (III) adsorption over the surface on Ce-CHT/PVA has been confirmed by Scanning electron microscopy and Energy dispersive X-ray spectroscopy (SEM-EDAX), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The quantitative estimation of As (III) has been carried out by Flameless Atomic Adsorption Spectrophotometer- Hydride Generator (AAS-HG) system. The As (III) adsorption efficiency of Ce-CHT/PVA composite nanofibers has been established as a function of pH, time, temperature and adsorbent dose. The adsorption data were best fitted to Langmuir isotherm and maximum adsorption capacity (q_m) was found to be 18.0 mg/g. The interference studies of several ionic species individually as well multi-element for As removal have also been reported. The measurement of uncertainty for As (III) determination was calculated after ascertaining the contributing factors. The data reported are with 95% confidence level (K=2). The Ce-CHT/PVA composite nanofibers are non toxic and can be used for water purification as such or after embedded in the form of membrane or candles.

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1. Introduction

The natural as well as anthropogenic contamination of metallic element in the environment as per United State-Environmental Protection Agency (US-EPA) are of major concern because of their toxicity, bio-accumulating tendency, threat to human life and environment.[1-3] The most common metallic elements for human poisoning are mercury, cadmium, lead, arsenic, chromium, copper and zinc. Some of them are carcinogenic. Arsenic (As)-a metalloid, is highly toxic and causes Neurologic, Cardiovascular, Gastrointestinal and Hepatic, Dermal disorder in human beings. Several diseases in human being like 'Kai Dam' in Thailand, 'Bell Ville' in Argentina, 'Black Foot' in Taiwan, tummy bug, cancers of lungs and skin, are caused by consumption of As contaminated water.[4] The As can exists in natural water both in inorganic and organic forms. In natural water it exists in two oxidation states, arsenite (As-III) and arsenate (As-V). The inorganic As is 70 times more toxic than organic species and within the class, As (III) is ten times more toxic than As (V).[5-6] It enters in the environment and water through geochemical reactions, industrial waste discharge, etc. The long-term consumption of As contaminated water causes harmful impacts on human being. According to the European Commission and US-EPA, the permissible maximum limit of As in drinking water is 10 μg/L. [7]

To overcome the problem of As in drinking water, various technologies such as oxidation, filtration, coagulation, ion exchange, adsorption and membrane separation [8, 9] have been employed. It has been observed that removal of As (III) is more tedious than As (V) by filtration.[10] The adsorption processes are commonly developed owing to their simplicity and ease in handling. The common adsorbents for arsenic removal include oxides of iron,[11-12] iron-impregnated chitosan,[13] aluminum compounds, sand, activated carbon,[14] silica ceramics,[15] Ce–TiO_2 adsorbent,[16] urchin-like α-FeOOH hollow spheres[17] and nanostructure material like graphene based hybrid for electrocatalyst. [18] In recent times, biopolymers like chitin and chitosan (CHT) etc, are being considered as suitable low cost adsorbents for the removal of heavy metals due to their biocompatibility, biodegradability and hydrophilicity.[19] Chitosan has emerged as biomaterial of choice for several applications based on its film-forming capabilities, metal-binding capacity, biodegradability, antimicrobial activity and wound healing capacity.[20] The positively charged amino group over CHT at pH 6 reacts with negatively charged metals ions and microbes. [21-23] The CHT can be transformed into chitosan beads, [24] iron-impregnated chitosan, porous chitosan/Fe_3O_4/Fe $(OH)_3$ microsphere,[25] iron-chitosan composite granules,[26] alpha-Fe_2O_3 impregnated chitosan beads,[27] chitosan-Fe-cross linked complex[28] and Ce-loaded cation exchange resins[29] for purification of water specially As (III). While the As (III) adsorption capacity of CHT is quite low, it requires longer exposure duration for effective adsorption in comparison to other adsorbents reported in literature.

Therefore, Ce (III) is loaded in the composite nanofiber to improve the adsorption capacity and reduction in adsorption time of CHT. It is observed that due to smaller ionic radii, high electric charge and higher potential energy associated with Ce, the adsorption behavior of Ce-CHT/PVA composite nanofibers increases significantly while the optimal exposure time was also reduced drastically. On addition of Ce (III) in CHT/PVA, the stability and attracting capability of composite nanofibers towards anionic species increases due to increase in the positive charge on surface of composite nanofiber.[30] However, due the crystal formation and H-bonding in D-glucosamine unit of CHT, it is difficult to electrospun fibers from the highly viscous solution.[31, 32] To reduce the viscosity of chitosan, polyvinyl alcohol (PVA) is added. The PVA reduced intermolecular interactions between the chitosan molecules and facilitated electrospinning. Furthermore, PVA is water soluble, non-toxic, and has good biological activities in combination with chitosan.[33] The present work reports preparation of Ce-CHT/PVA composite nanofibers by electrospinning and studies on adsorption and removal of As (III) from water.

2 Experimental and Characterization

2.1 Materials

Analytical reagents grade chemicals like, Chitosan (M.W;100000-300000) from Across Organic, Polyvinyl-alcohol, (M.W; approx. 125000) from CDH, formic acid, Cerium (III) nitrate hexahydrate, (M.W;434.23) from Chemica-biochemica reagents, Sodium borohydride ($NaBH_4$), Hydrochloric acid (HCl), Sodium hydroxide (NaOH), Potassium nitrate (KNO_3) and Potassium hydroxide (KOH) from E. Merck (India) were used. Double distilled water was used for synthesis work while de-ionized water of 18.2 m Ω resistivity (Millipore, USA) was employed for analysis on Atomic adsorption spectrophotometer-hydride generator (AAS-HG).

2.2 Synthesis of Ce-CHT/ PVA composite nanofibers by Electrospinning

The Ce-CHT/ PVA composite nanofibers were prepared by using electro spinning equipment (ESPIN-NANO, procured from Physics Instrument Company, Chennai) at optimized processing parameters discussed in earlier studies.[34-36] For the preparation of Ce-CHT/PVA composite nanofibers, 4 wt % of CHT was dissolved in 2% (v/v) formic acid with continuous stirring for 24 hr at room temperature using magnetic stirrer. The 8% solution of PVA in acetic acid (2%, v/v) was added to the clear solution of CHT in the ratio of 7:3 (PVA: CHT) with continuous stirring for 4-5 hrs. In CHT/PVA solution, Cerium (III) nitrate hexa-hydrate (1-6; w/w %) was added with continuous stirring for 4-5 hrs. The resultant Ce-CHT/PVA solution was filled in 2mL syringe, electrospun at applied 2kV voltage and 0.2 ml/h flow rate. The distance between syringe tip and collector was maintained at 20 cm. The composite nanofibers were collected on aluminum foil wrapped on collector. The Ce-CHT/PVA composite nanofiber prepared by this route exhibits hydrophilicity and some nanofibers disintegrate in water. To overcome this problem, the composite nanofibers were heated in an oven at 85^{o}C for 120 minutes.

2.3 Characterization

The morphology of Ce- CHT/PVA composite nanofibers before and after As (III) adsorption was studied by scanning electron microscope (SEM Model EVO M-1of Ziess), which was equipped with Energy Dispersive X-ray Spectroscopy (EDAX) for measurement of elemental composition. The functional groups present on the surface of composite nanofibers were investigated by FTIR spectrophotometer (Nicolet make, Nexus-47). The X-ray diffraction patterns of composite nanofibers before and after adsorption were recorded on X-Ray Diffractometer (Model-Expert D6, Japan), at wavelength 1.5404 Å and 2θ angel between 5 to 80^{0}. The concentration of As(III) in solution after adsorption with Ce- CHT /PVA composite nanofibers were analyzed using AAS-HG, (Model Vario-6-Analytik Jena, Germany) at wave length 193.7 nm. AAS-HG was calibrated using NIST (USA) make SRM- 3103a. For all As (III) adsorption studies on composite, CSIR-NPL make reference standard were used (CSIR-NPL is custodian of measurement standards in India). The VHG (UK) make Multielement SM-75-100 standard reference material was used to check the mixed inference of various ions. All the reference solutions were used after subsequent dilutions. The individual solutions of various ionic species used in interference studies were prepared from high purity metals/salts. The UV-Vis spectrophotometer (Hitachi, Model-U3900H) was used to further establish the efficacy of removal of As(III) from water.

2.4 Determination of point zero charge (pH_{PZC})

The pH_{PZC} of Ce-CHT/PVA was determined using potentiometric titration[37] in nitrogen medium. 0.025g of composite nanofibers were mixed in 25 mL of 0.03M KNO_3 solution and system was kept overnight (24 hrs) under constant stirring to stabilize pH. Subsequently, 0.1 mL of 1 M KOH was added to the stabilized the system. The pH was recorded after each addition of 0.05 mL solution of 0.1M HNO_3 using micropipette. Blank titration (0.03M KNO_3) was also carried out in similar manner. The pH_{PZC} was determined from the curve of pH against acid consumed (Fig.1 'a').

2.5 Adsorption Experiments

The adsorption experiments for the removal of As (III) were carried out by suspending composite nanofiber with desired concentration of As (III) solution. The stock solution of As (III) was diluted in the desired range and pH was adjusted with the help of 0.001M HCl and NaOH solutions. The solutions along with Ce-CHT/PVA composite nanofibers were stirred on magnetic stirrer at very low speed. The composite nanofibers can be easily separated from solution without any filtration device. Finally each samples were analyzed for remaining As(III) concentration by AAS-HG using 3% sodium borohydride, 1.5 % NaOH and 2% HCl for arsine generation. The arsine atomize at 900°C using electro-thermal heating in presence of argon gas having 36 ml/min flow rate. [38] The adsorption capacity (q_e) of Ce-CHT/PVA composite nanofibers for removing As (III) was calculated by eq.1, whereas % removal of As (III) by composite nanofibers was calculated by eq.2.

$$\text{Adsorption capacity } (q_e) = \frac{(C_i - C_f) * V}{m} \qquad \text{------ (1)}$$

$$\text{\% Removal of arsenic (III)} = \frac{(C_i - C_f) * 100}{C_i} \qquad \text{------ (2)}$$

Where, 'C_i' and 'C_f' was the initial and final concentration of As (III) solution (mg/L), V; volume (L) used and m is the weight of composite nanofibers (g).

The effect of pH on adsorption As (III) by Ce-CHT/PVA has been studied and illustrated in Fig.1 (b). It can be observed that As (III) is mainly adsorbed in the pH range of 6.2-7.0. Any increase or decrease of pH of test solution accompanies the decrease in adsorption capacity of Ce-CHT/PVA. Deforming of nanofibers at lower pH values could be one of the reasons for decrease in adsorption at lower pH values besides pH_{pzc} of the composite.

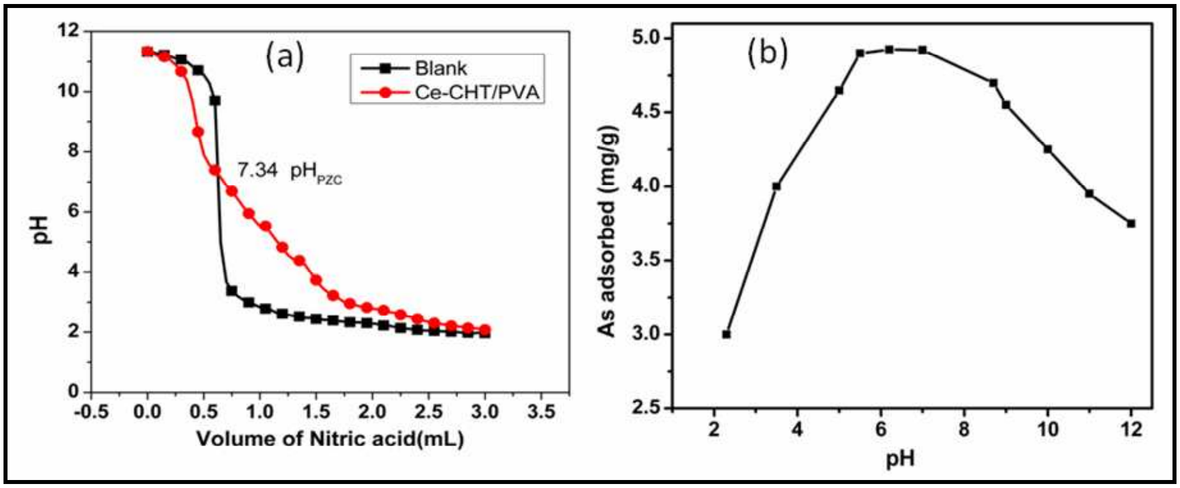


Fig.1: (a) Potentiometric curve for pH $_{PZC}$ determination and (b) Effect of pH on As (III) adsorption

The adsorbent dose of Ce-CHT/PVA composite nanofibers is varied (2-20 mg/50 ml) while keeping fixed concentration of As (III) in solution. 2 mg of Ce-CHT/PVA composite nanofibers are stirred in 50 ml solution with fixed quantity of As (III). Fig.2 illustrates the effect of adsorbent dose on adsorption of As (III). The maximum adsorption is observed for 2 mg of nanofibers, which gradually decreases on increasing weight of Ce-CHT/PVA composite nanofibers. The maximum adsorption observed for 2 mg composite sample may be attributed to easy accessibility of free active sites on surface of material. On increasing weight of Ce-CHT/PVA, the number of active sites increases but ratios of As (III) to active sites decrease resulting in gradual decrease of adsorption. The optimum dose for As (III) is observed to be about 10mg/50mL for 3.5 mg/L of As (III) solution.

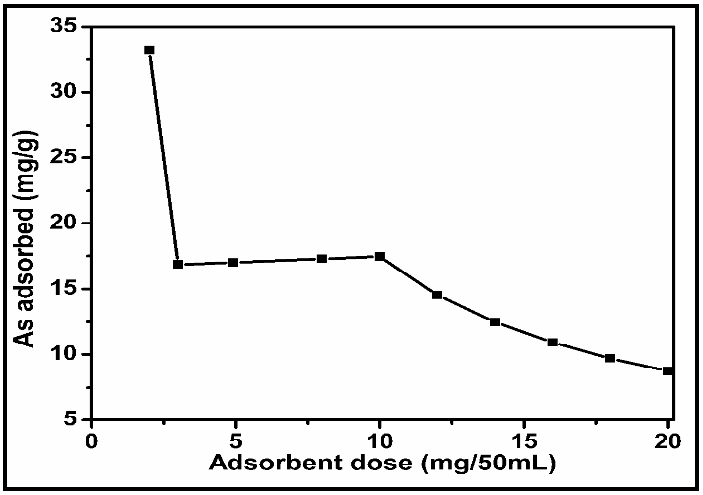
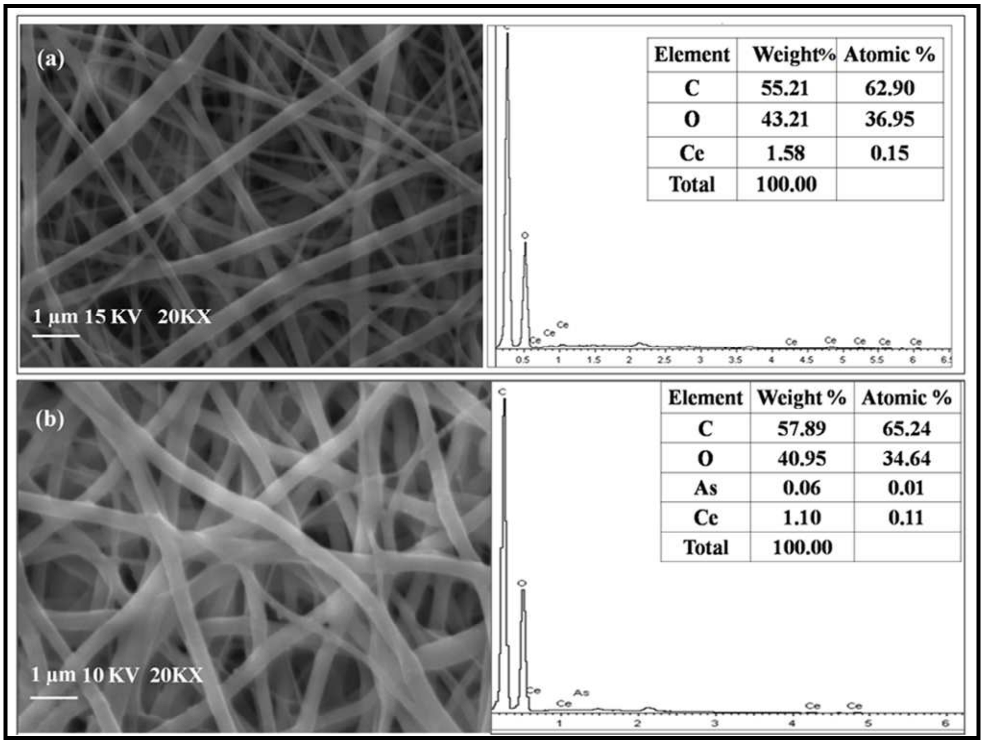


Fig. 2: Effect of Adsorbent dose on As (III)

3.0 Results and Discussion

3.1 Morphology of composites nanofibers by SEM and EDAX

Chitosan is a linear cationic biopolymer soluble in most of the acids and protonation of chitosan changes it into a polyelectrolyte thus increasing the viscosity. The repulsive forces between ionic groups within polymer backbone, arising due to the application of high electric field during electrospinning, restrict the formation of continuous nanofibers and often produce beads, [39] which makes it difficult to fabricate pure CHT nanofibers. Therefore, to control the intermolecular interactions between the CHT molecules, PVA polymer is added to control the viscosity of solution. After optimizing various electrospinning parameters, bead free nanofibers were prepared by employing PVA to Chitosan in the ratio of 7:3. After CHT/PVA polymer fabrication, varying weight fraction of Cerium (III) nitrate hexahydrate (0.5% to 5 wt %) were added to get Ce rich nanofibers. It is observed that at 3.5 wt %, Cerium(III) nitrate hexahydrate in CHT/PVA solution gives bead free continuous composite nanofibers. To confirm the adsorption of As(III) on the Ce-CHT/PVA nanofiber, the samples were analyzed for elemental distribution by EDAX and elemental mapping **(Supplementary information as Fig. S1)**.



Element	Weight%	Atomic %
C	55.21	62.90
O	43.21	36.95
Ce	1.58	0.15
Total	100.00	

Element	Weight %	Atomic %
C	57.89	65.24
O	40.95	34.64
As	0.06	0.01
Ce	1.10	0.11
Total	100.00	

Figure 3: SEM and EDAX of Ce-CHT/PVA composite nanofibers (a) before and (b) after Adsorption

It is observed that all the elements are uniformly distributed throughout Ce-CHT/PVA composite sample. EDAX of Ce-CHT/PVA composite nanofiber [Fig.3(a)] show the presence of C, O and Ce only. However, Ce-CHT/PVA composite nanofibers, after adsorption of As (III), indicate the presence of As along with C, O and Ce [Fig. 3(b)]. A comparison of Fig.3 (a) & (b) also reveals the change in morphology of Ce-CHT/PVA composite nanofibers after As (III) adsorption.

3.2 Effect of pH, Concentration of Ce (III) and temperature on adsorption of As (III)

The pH and pH_{pzc} of a solution have a significant effect upon adsorption at the liquid-solid interface. Arsenic can exist in several oxidation states like (-3, 0, +3 and +5), however in natural water, it exist in inorganic form as oxyanions of trivalent arsenite or pentavalent arsenate. The effect of pH on % removal of As (III) has been investigated by varying pH from 2-12. As shown in Fig.1(b), on increasing pH of test solution from 2 to 6.2, removal of As (III) increases continuously, while on increasing pH (above 7.0) adsorption of As(III) shows gradual decrease. The point zero charge of Ce-CHT/PVA composite nanofiber is found to be 7.34 [Fig.1 (a)]. At pH less than pH_{PZC} (7.34) the surface of adsorbent would considered to be positively charged and therefore would involve in protonation of $–NH_2$ group, resulting in attracting oxyanions of As. However at pH above pH_{PZC} the surface of adsorbent is considered to be negatively charged and attract cations. As shown in Fig.1(b), the maximum adsorption was observed in pH range (6.2-7.0). At this pH range (6.2-7.0), $-NH_2$ groups of Ce-CHT/PVA nanofibers are positively charged and involve in protonation of amino group ($-NH_2$ to NH_3^+), which leads to the interaction of As (III), while at basic pH, protonation does not occur and as a result the adsorption decreases. The pH of test solution is tested before and after adsorption of As (III) and it is observed that there is no significant change in pH. Therefore it can be inferred that Ce-CHT/PVA composite nanofiber is insoluble in water.

The effect of various concentration of Ce(III) nitrate hexahydrate (0.5-5%) in CHT/PVA composite nanofibers for As (III) removal is investigated at ambient temperature. As shown in Fig.4, the adsorption of As (III) increases on increasing concentration of Ce (0.5 to 3.5 %) in CHT/PVA composite nanofibers. This happens because on increasing concentration of Ce (III), the positive charge on chitosan increases. Above 3.5 weight % of Ce (III) in CHT/PVA, viscosity of solution is increased, resulting in formation of beaded and non uniform Ce- CHT/PVA composite nanofibers, resulting in decreased adsorption of As (III).

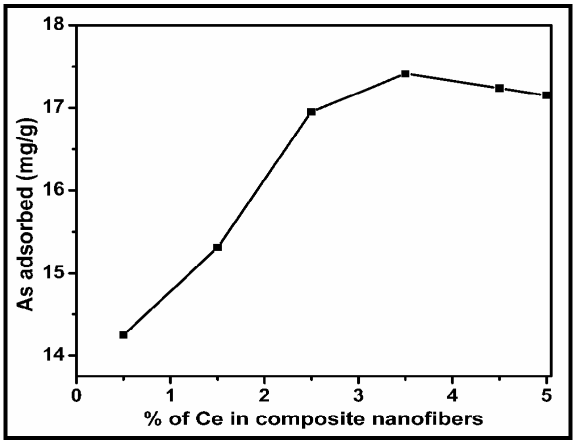


Fig.4 Effect of % Ce As (III) adsorption

The effect of temperature on As (III) adsorption is investigated by varying temperature (10-65°C) at optimized pH. The maximum adsorption observed as shown in (supplementary information as Fig. S2) is between temperatures 20-35°C. Increasing in temperature (>35 °C) or decrease (<20 °C) results in decrease in As (III) adsorption. This could be attributed to protonation of -NH$_2$ groups, which remain unaffected probably due to the surface complexes and interactions.[40]

Figure S3 shows FTIR spectra of CHT/PVA, Ce-CHT/PVA and As (III) adsorbed Ce-CHT/PVA composite nanofibers. The shifting of adsorption peaks at 1363 cm^{-1} & 1075 cm^{-1} [Fig. S3 (a)] toward higher wave numbers at 1371 cm^{-1} & 1095 cm^{-1} [Fig S3 (b)] may be due to interaction of -NH group with cerium (III) in Ce- CHT/PVA.[30] After adsorption of As (III) (curve 'c', Fig.S3), it is observed that the peak intensity increases, due to the interaction of As(III) with -NH$_2$ (1643 cm^{-1}, 1579 cm^{-1}) and Ce (1376 cm$^{-1,}$ 1095 cm^{-1}).[40-42] From the Figure, it is deduced that the peak positions shifts towards higher wave number after adsorption of As (III) on the Ce-CHT/PVA composite nanofibers surface.

In XRD spectra (Supplementary information as Fig.S4) of Ce-CHT/PVA shifting of absorption peaks from 9.16 ° and 19.32°[43-44] in (Fig.S4, curve a) to 2θ= 9.3° and 19.86° (Fig.S4, curve 'b'), confirming the As (III) adsorption on Ce-CHT/ PVA composite nanofibers. The literature reveals that peaks at 34° and 37° are due the Ceria structure.[45] The peaks at 38° and 45° may have appeared due the introduction of cerium in CHT/PVA matrix resulting in formation of unknown crystallite phases. The results are in agreement with observation of SEM and FTIR.

On the basis of SEM-EDAX, FTIR and XRD studies, it is evident that Ce-CHT/PVA interacts with As (III) on -NH and Ce (III) sites. The electrospun composites nanofibers of CHT, PVA and Cerium (III) may be considered as formation of complex of chitosan with PVA and Ce (III). In acidic solutions, more positively charged surface sites are developed by the protonation of amino groups on chitosan and the highly electropositive Ce (III), which attract the As(III) efficiently. A graphical representation of the Ce-CHT/PVA composite nanofibers interacting with As (III) is given in Fig.5. The adsorption studies are carried out in pH range (6.2-7.0). CSIR-NPL certified reference material was used for As removal studies. The CRM is made in nitric acid after dissolving high purity arsenic oxide powder. The NIST (USA) certified reference material is used for calibration of equipment which is prepared in nitric acid. The H_3AsO_3 is neutral species (pH<9.2) and within 6.2-7.0 pH range , As (III) interacts with $-NH_2$, and Ce (III) group attached to Ce-CHT/PVA and adsorbed over surface of composite nanofibers.[46] It is also evident from FTIR results **(supplementary fig. S3)**, the adsorption peaks at 1643 cm^{-1} and 1579 cm^{-1} in curve 'b' shifted to 1656 cm^{-1} in curve 'c', confirms the adsorption of As (III) on the surface of Ce-CHT/PVA composite nanofibers. The increased in intensity of FTIR peaks in case of adsorbed Ce-CHT/PVA nanofibers (**supplementary fig. S3)** is also an indication of adsorption of As (III) on composite surface.

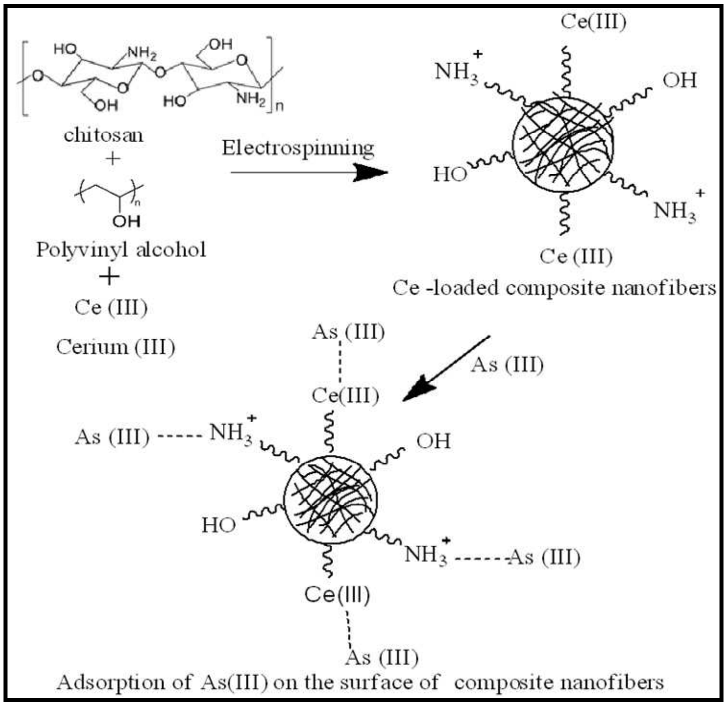


Fig.5: Probable reaction mechanism of As (III) adsorption on Ce-CHT/PVA composite Nanofibers.

3.3 Kinetic study:

The kinetic study of adsorption of As (III) on Ce-CHT/PVA composite nanofiber is carried out to evaluate equilibrium time required for process and the rate of adsorption of As (III) on Ce-CHT/PVA composite nanofibers. The experiments are carried out with 3.5 mg/L concentration of As (III) at optimized conditions. The results of kinetic studies are given in Fig.6. From the figure, it is observed that adsorption of As (III) gradually increases and more than 98% adsorption occurs within 60 minutes. But in the first ten minute, the removal of As (III) was faster in comparison to further increase in time, probably owing to availability of more free sites in Ce-CHT/PVA composite nanofibers. Adsorption rates gradually turns slow because of increased occupancy of free sites by As (III). The maximum adsorption occurs within first 60 minute and after that the adsorption of As (III) becomes stagnant. Fig.6(a) represents the effect of time on adsorption capacity (‘t’ vs. ‘q_t’), whereas Fig.6(b) express the regression curve (t/q_t Vs ‘t’). The adsorption capacity (q_e), initial adsorption rate (h), rate constant (k) and coefficient of determination (R^2) is obtained from the linear graph between ‘t/qt’ and time. Pseudo second order kinetic equation used is given as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_t} \qquad \text{------ (iii)}$$

When ‘t’ equal to zero initial adsorption rate ‘h’ may be calculated as:

$$h = kq_e^2 \qquad \text{------ (iv)}$$

where ‘q_e’ and ‘q_t’ are the adsorption capacity of As (III) in ‘mg/g’ at equilibrium and at time ‘t’ respectively. The ‘h’ represents the initial adsorption rate ($mg/g^x min$). and ‘k’ represents the rate constant ($g/mg^x min$). The adsorption capacity ‘q_e’ of the prepared Ce-CHT/PVA composite nanofibers was determined, which was ca. 17.54 (mg/g). From the regression graph, the value of ‘h’, ‘k’ and R^2 are found to be 12.19 mg/g.min, 0.04 g/mg.min and 0.999, respectively. It can be concluded from the results that the adsorption process of As (III) by Ce- CHT/ PVA composite nanofibers fits to Pseudo-second order kinetic model.

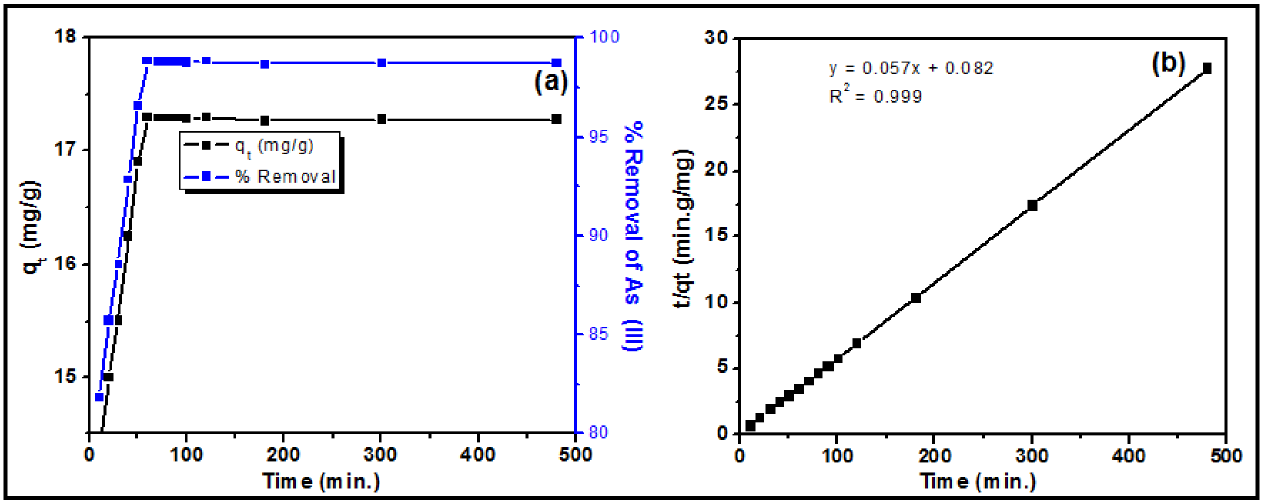


Fig.6: (a) Effect of time on adsorption capacity of As (III), (b) Pseudo second order kinetics

3.4 Adsorption Isotherm Model:

There are different adsorption isotherm models for understanding solid-liquid interface, such as Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherm. Out of these, Langmuir and Freundlich are most commonly used models for verifying the relationship between solid-liquid interfaces.[47] The equilibrium studies are carried for 10 mg of Ce-CHT/PVA composite nanofibers in 50 mL solutions, where as the concentration of As (III) is varied from 100-4500 µg. After 60 minutes, the remaining concentrations of As (III) 'C_f' were measured. Fig.7 (a) indicates that As (III) adsorption capacity of Ce-CHT/PVA increases gradually on increasing the concentration of As (III). It is further observed that 10 mg of Ce-CHT/PVA removes upto1500 µg/L concentration of As (III) and maximum adsorption capacity 'q_m' are observed at 3500 µg/L concentration of As(III). No further adsorption takes place on increasing concentration of metal ion due to saturation of active sites in Ce-CHT/PVA composite nanofibers. The findings of the present study were applied to Langmuir isotherm model, which is based on the assumption that interactive force between the adsorbed molecules is negligible and once the active site is filled, no more adsorption takes place. The Langmuir isotherm equation[27, 48] used for calculation is:

$$\frac{C_f}{q_e} = \frac{1}{K_L\, q_m} + \frac{C_f}{q_m} \qquad \text{----- (v)}$$

Where 'q_e' (mg/g) is the amount of the As(III) adsorbed on Ce-CHT/PVA composite nanofibers, 'C_f' (µg/L) is the final concentration of As(III) remaining in the test solution, 'q_m' is the maximum adsorption capacity in mg/g, 'q_e' (mg/g) is the adsorption capacity at equilibrium, K_L(L/mg) is the energy of reaction. The value of 'q_m' (maximum adsorption capacity) and 'K_L' (energy of reaction) can be determined by slope and intercept of a linear plot of C_f/ q_e against 'C_f', as shown in Fig.7 (b). The maximum adsorption capacity of the composite using Langmuir isotherm is found to be 18.0 mg/g, whereas 'K_L' and 'R^{2}' are observed to be 0.12 L/mg and 0.999, respectively. The experimental data fitted to Langmuir isotherm suggests the monolayer adsorption of As (III) on the surface of Ce-CHT/PVA composite nanofibers. The adsorption behavior of CHT/PVA composite nanofibers is also studied by varying initial concentration of As (III) (100-4500µg/L) at optimized condition. The observed efficiency was only 30-35%. Effect of initial concentration on As (III) adsorption and Langmuir isotherm demonstrate that adsorption capacity of CHT/PVA composite nanofibers is quite low (Supplementary information as Figure S 6).

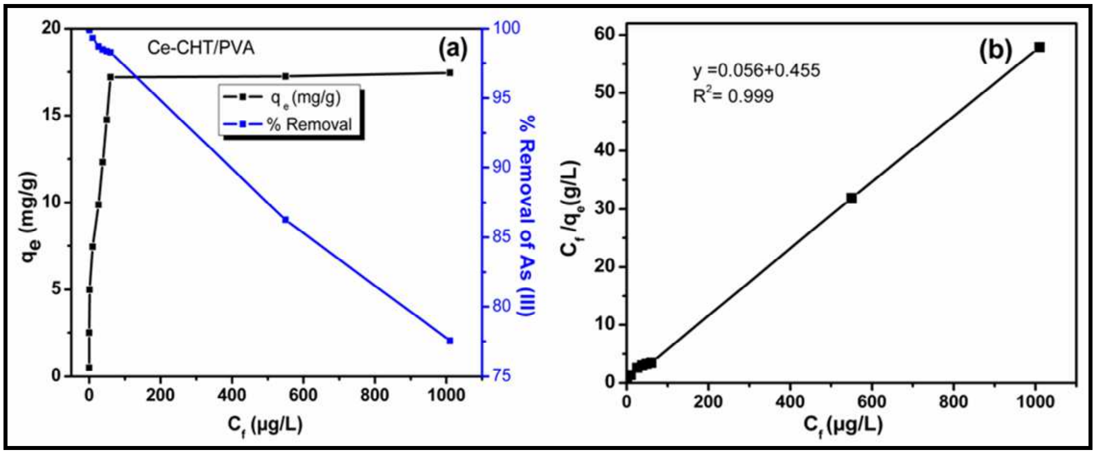


Fig.7: (a) Effect of initial concentration of As (III) on adsorption and (b) Langmuir adsorption isotherm of Ce-CHT/PVA composite nanofibers.

The separation factor 'R_L' is an important feature of Langmuir isotherm to check the feasibility of process, which was calculated using equation (vi).

$$R_L = \frac{1}{1 + 1\,(K_L C_i)} \qquad \text{----- (vi)}$$

Where: C_0 = initial concentration K_L = Langmuir Constant; energy of adsorption. R_L value indicates whether adsorption nature is unfavorable (>1), linear (=1), favorable (>0 or <1) and irreversible (=0). In the present study, the value of R_L calculated from equation-(vi) is found to be 0.90 which is (>0 or <1), suggests favorable adsorption of As (III) on the surface of Ce-CHT/PVA composite nanofibers.

The quality assurance is an important aspect for determination of toxic species like arsenic. The quality and reliability of data depends upon measurements of uncertainty of each step involved during measurement. There are many steps in the quantification of As (III) by AAS-HG like-repeatability, weighing, reference material, volumetric flask, pipettes, etc. The calibration of AAS-HG has been done using NIST-SRM (9.999 ± 0.015 mg/g) following appropriate dilutions in the range of analyte sample. A process blank was also done and corrections applied wherever required. Mean concentration values of triplicate for each sample are considered for calculation of As (III) concentration. The major sources of uncertainty have been included in the combined uncertainty according to EURACHEM/GUM guidelines. [49-50] For example the measurement uncertainty for 1000 µg/L As (III) standard solution has been done and potential sources (as given in Table-1) are considered for combined uncertainty. On the basis of measurement, the results for 1000 µg/L standard solution are found to be 999.6± 5.4 (µg/L) with 95% confidence level (K=2) as given in Table-1. In the same manner, various concentration of As (III) are considered and same parameters are considered for final calculation.

Table-1: Major sources of uncertainty in the measurement of As (III) by AAS-HG.

Parameters	**Value; x**	**Unit**	**Standard Uncertainty; u(x)**	**unit**	**u(x) /x**	**U_c (K=2)**
Repeatability	999.6	µg/L	0.310	µg/L	0.00031	2.7
NIST SRM, 3103a	9.999	mg/g	0.015	mg/g	0.0015	
Volumetric Flask	50	mL	0.01	mL	0.00020	
Weighing Balance	0.1	g	0.0001	g	0.00100	
Pipette; Suction	5.0	mL	0.01	mL	0.00200	

The proposed material (Ce-CHT/PVA composite nanofiber) are compared with other chitosan based adsorbents cited in the literature (Table-2). It could be seen from the table that proposed material have several advantages in terms of speed and efficiency of As(III) adsorption in comparison to those cited in literature.[14, 24-29]

Table 2: Adsorption comparision of Ce-CHT/PVA composite nanofibers and cited adsorbent

Name of adsorbent	**Adsorption capacity (mg/g)**	**Time**	**pH/ Temp.**	**Ref.**

Iron-impregnated chitosan	6.48	2 hrs	8/25	14
Chitosan beads	1.83	24 hr	5/25	24
Porous CS/ Fe_3O_4 / $Fe(OH)_3$ microsphere	8.47	45 min	No information	25
Iron-Chitosan Composite granules	16.15	4 hr	7/25	26
Alpha-Fe_2O_3, impregnated chitosan beads	6.18	6 hrs	5/30	27
Chitosan-Fe-crosslinked complex	13.4	60 min	9/25	28
Cerium-loaded Cation Exchange resin	2.59	No information	5-6	29
Ce-CHT/PVA Composite Nanofibers	18.2	60 min	6.2-7.0/(20-35°C)	Present study

3.5 Interference studies:

The performance of Ce-CHT/PVA composite nanofibers (10mg) for As (III) removal is carried out individually for Mg, Ca, Pb, Zn, Cu, Fe, NO_3^-, Cl^- and SO_4^- ions. Equimolar quantity of each ion with As (III) were taken. The assessment was carried out with 50 ml analyte solution at 6.2-7.0 pH range. The results are presented in Table-3.

Table -3: Removal of As (III) in presence of individual ions

Ionic species used for interference studies	Initial concentration of As (III) (µg/L)	Concentration of ions added (µg/L)	Remaining concentration of As (µg/L) in presence of interfering species
As without ions	1000	0.00	1.0
As with Pb	1000	1000	28.3
As with Mg	1000	1000	1.4
As with Ca	1000	1000	3.6
As with Zn	1000	1000	12.3
As with Cu	1000	1000	13.5
As with Cl^-	1000	1000	11.2
As with NO_3^-	1000	1000	23.8
As with SO_4^-	1000	1000	38.4

From the table it is observed that Pb, NO_3^-, and SO_4^- compete with As (III) during adsorption, whereas Ca, Zn, Mg, Cu and Cl^- show less interference. However, the composite fibres show higher selectivity towards As (III). Further, As (III) removal experiment was also carried out for As (III) solution having multi elements (total 800 μg/L or 100 μg/L each) at optimized conditions. In this experiment, the As (III) adsorption on Ce-PVA-CHT composite nanofibers is found to decrease by 25-35% indicating interference by other ions.

3.6 Recycling of adsorbent:

To check the reusability of Ce-CHT/PVA composite nanofibers, the test material was regenerated and used twice. Regeneration involved treating the fiber with 0.01M HCl followed by thorough rinsing with de-ionized water. Initially the prepared composite nanofiber removes As (III) completely. However, in second and third cycle, the As removal dropped to 65%, 35%, respectively. The reduction in adsorption could be attributed to deformation of nanofibers in HCl medium during regeneration.

The quality of water, before addition of adsorbent and after removal of As (III), is assessed by obtaining UV visible spectra (supplementary information Fig .S5 (a) & (b)). No peak was observed at 272 nm after removal of As (III). UV-Vis spectra thus conclude that a Ce-CHT/PVA composite nanofiber removes As (III) efficiently. This information further supports the findings of AAS-HG.

4. Conclusions

In the present investigation, Ce-CHT/PVA composite nanofibers prepared through electrospinning technique showed efficient removal of As(III) from water. The proposed material is having high surface area and more active sites for As (III) adsorption in comparison to other adsorbents reported in literature. SEM-EDAX, FTIR and XRD also confirm the As (III) adsorption over the surfaces of Ce-CHT/PVA composite nanofibers. The kinetic study of adsorption reveals that more than 80 % of As (III) can be removed within first 10 minutes. The experimental data follows Langmuir isotherm model with adsorption capacity 18.0 mg/g. The value appears to be better than the several other chitosan based adsorbents. The quality of water was further confirmed by UV-Vis spectroscopy, before and after As (III) removal. The effect of several common ions present in water viz; Mg, Ca, Pb, Zn, Cu, SO_4^-, NO_3^-, Cl^- on adsorption of As (III) was checked individually and with multi-element solution. The results show favorable selectivity for As (III). Therefore, it may be concluded that the proposed material can be used for arsenic removal in presence of several tested ionic species efficiently. The literature further reveals that majority of the adsorption processes required one oxidizing and one adsorbing agent for removal of toxic elements, while the material under study adsorbs As (III) efficiently without presence of oxidizing agent. Therefore, water can be safely used for potability as well as other applications. The prepared material (Ce-CHT/PVA) purifies water below prescribed limit of WHO/EPA up to 1500 μg/L. Besides, Ce-CHT/PVA composite nanofibers are nontoxic and can be used for water purification as such or after embedding them on non-woven fabrics, porous membranes or candles. Because of rapid and high adsorption of As (III), such materials can be useful in areas having no access to electricity.

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Figure Captions:

Figure1:(a) Potentiometric curve for pH $_{PZC}$ determination (b)Effect of pH on As (III) adsorption.

Figure 2:Effect of Adsorbent dose on As (III) adsorption.

Figure 3: SEM of Ce-CHT/PVA composites nanofibers (a)before and (b)after adsorption.

Figure 4: Effect of Ce concentration in CHT/PVA composite nanofibers on As (III) adsorption.

Figure 5:Probable reaction mechanism of As (III) adsorption on Ce-CHT/PVA composite nanofibers.

Figure 6:(a) Effect of time on adsorption capacity (q_e) of As (III), (b) Pseudo second order kinetics.

Figure 7:(a) Effect of initial concentration of As (III) on adsorption and (b) Langmuir adsorption isotherm for Ce-CHT/PVA composite nanofibers