Carbon-Based Adsorbents from Naturally Available Bermuda Grasses: Removal of Total Dissolved Solids and Arsenic Ions

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Abstract

In the present study, we have reported the synthesis of nano porous carbon material (GC) by the thermal treatment of the commonly available Bermuda grasses, and metal oxides doped biocompatible polymer chitosan-GC based porous cross-linked composites (CHGCCZ) as adsorbent materials for the removal of total dissolved solids (TDS) and efficient removal of arsenic (As(V)) ions from aqueous medium, respectively. The synthesized adsorbents have been characterized by FTIR, PXRD, FESEM, TGA, and the systematic investigations have shown that the incorporation of GCs into cross-linked matrix makes them porous, more resistant to degradation, and suitable adsorption matrix for the toxic As(V) removal. The presence of As(V) ions is quantified by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) measurements. The amount of TDS and arsenic concentration was reduced to the minimum value of 103 ppm (average value '119 ppm) from 414 ppm and 7.7 ppm from very high concentration of 10.15 ppm, respectively. The recyclability test has also been performed after regeneration of the CHGCCZ and the initial findings has been found to be promising. Therefore, we have systematically investigated the efficacy of TDS removal by GCs and As(V) adsorption properties of metal oxide doped cross-linked CHGCCZ composite from the aqueous system and demonstrated the regeneration process for CHGCCZ in our study.

Keywords: adsorption, arsenic removal, biocompatible, chitosan, total dissolved solids

Introduction

Water is considered as the most important and essential component of biological systems. The scarcity of pure drinking water poses an important environmental aspect. Heavy metal pollution, dye contaminants, drugs, pesticides and excessive amount of total dissolved solids (TDS) cause severe water crisis and attract serious attention towards the most important issues in the current era. [1-4] Metallurgy, printing, textile, mining, and pharmaceutical industries are the robust producers of these pollutants and contaminants. An elevated level of TDS, in drinking water, by itself, does not indicate the health risk. However, elevated levels of specific compounds included in the TDS measurements, such as dyes, nitrates, arsenic, aluminium, copper, cadmium, chromium, or lead, could present health risks. [5-8] Organic dyes are also considered as serious pollutants as they can damage liver, digestive

and central nervous systems of human beings. Most of the heavy metal ions have adverse toxic and carcinogenic effects on human being even at very low concentration as they gradually accumulate in the body parts through the drinking water over the time. [9,10] Among all the heavy metal ions, nonbiodegradable ions especially Arsenic (As(V)) in potable drinking water cause acute global problem owing to their adverse impact on the environment and health.^[11-13] The arsenic contamination problem is especially acute in developing parts of the world where the water treatment infrastructure may not be capable of providing suitable treatment. Various types of physical, chemical, and biological techniques were employed in wastewater treatment.^[14-16] Elgarahy et. al. had shown that adsorbents such as monolithic algal green powder (MAGP),[17] Untapped Sepia Shell-Based Composite (SSBC)^[18] are suitable as an efficient biosorbent in terms of removal and recovery of cationic dyes from wastewater. These heavy metal contaminants in aqueous medium are usually discarded by the expensive methods based on ion exchange or chemical and microbiological precipitation such as ion exchange, [19] reverse osmosis, [20] microfiltration, precipitation, [21] cell culture and development of microorganisms^[22]. But, these methods are having limitations for high volumes, low metal concentrations, and low discharge limits. Among them, adsorption based methods are favourable for water remediation in terms of cost-effectiveness and simplicity. [23-28]

To date, an extensive amount of research has been carried out to explore a wide variety of adsorbent materials for the efficient removal of As(V) from potable water resources. [29,30] Among various adsorbents, carbon based nanomaterials are popularly accepted as novel adsorbents owing to their excellent thermal and mechanical properties, unique structure, reasonable wettability and excellent dispersibility in various solvents. [31-35] But, the easy and cost-effective synthesis of carbon based nanomaterials with high surface area and profuse nano pores remains an important and challenging aspect for applications like water filtration. [36] In line with this, cellulose (the most abundant renewable bio-polymeric structure consisting of both amorphous and crystalline domains) based adsorbent materials have been recently drawn a lot of attention for water remediation for their ion removal efficacy and cost-effective production. On further note, cellulose produce various forms of nanocelluloses, on treatment with acid or any other mechanical treatment, depending on the various preparation techniques and source elements.^[37-39] A point to be noted is that a large number of the adsorbent materials are also made of metal oxides/hydroxides dopents such as iron, aluminium, copper, zirconium and titanium etc. [40-42] Among them CuO attracts major attention as dopents and its effectiveness in removing As from drinking water is a major focus as CuO and Cu(OH)2 based adsorption sites have strong affinity towards arsenate. [43-46] It has been shown that CuO and encapsulating chitosan matrix adsorb arsenic by means of electrostatic attraction under controlled pH environment. Also, no significant interference by other anions present in water has also been reported for As(V) adsorption process by CuO-ZnO. [47] These reported studies confirm the significance of CuO-ZnO based adsorbents. In addition to this, CuO and ZnO have been demonstrated as good antibacterial agents.

Therefore, in the quest for suitable cost effective adsorbent material for removal of TDS, especially As(V), chitosan (a biopolymer and alkaline deacylated form of chitin) has emerged as the most favourable material of choice having properties such as biocompatibility, natural abundance and the presence of various functional groups (-OH, -NH₂) which take part as metal binding sites by means of ion exchange and chelation mechanism depending on neutral or acidic medium, respectively. Therefore, chitosan could be employed as useful material that has shown strong adsorption for As(V) and several other heavy metal ions. In this regard, Almughamisi *et. al.* have shown the employment of Cu(OH)₂ and CuO modified chitosan sorbents for the removal of Cr(VI) oxyanions from aqueous medium. Again, incorporation of carbon based adsorbents into the cross-linked chitosan structure which is known to effectively reduce TDS especially As(V) ions would

enhance the adsorption of As(V) owing to the improvement of number of binding functionalities and mechanical and thermal stability.^[52] In addition, ease of production of adsorbents would reduce the overall costing of As(V) removal.^[53] Therefore, developing an adsorbent containing CuO-ZnO doped cross linked chitosan cryogel structure would provide enhanced adsorption sites and additional thermal and mechanical stability.

Here, we demonstrate the synthesis of carbon-based adsorbent material from commonly available grass (GC) by thermal treatment of the grass and its application for easy, effective and high volume quantity water purification purpose. We have further prepared CuO-ZnO doped carbon adsorbent containing cross-linked chitosan composite (CHGCCZ) for efficient removal of As(V) from portable water. We have also prepared only GC containing cross-linked chitosan composite (CHGC) in order to understand the role of CuO-ZnO in CHGCCZ in case of As(V) removal. The synthesized GCs and their composite material have been further characterized by FTIR, TGA, FESEM, and PXRD and employed mainly for the efficient As(V) removal as our studied adsorptive material and recycled to check its suitability for number of cycles. The concentration of As(V) has been measured by means of Inductively Coupled Optical Emission Spectroscopy (ICP-OES) analysis. Therefore, we have demonstrated thermally treated grass materials based cost-effective adsorptive material for the successful removal of As(V) in our study.

Results and discussion

Scheme 1. Synthesis scheme for the preparation of CuO and ZnO doped porous cross-linked Chitosan-GC composite (CHGCCZ) material.

The detailed synthesis procedures for the studied materials, namely GC. CHGC and CHGCCZ, have been described in the supporting information. The synthesis scheme for chitosan based CHGCCZ composite material is given in Scheme 1. Figure 1a-d have shown FTIR spectrum, PXRD pattern, Raman spectrum, and pore volume Vs radius plot obtained from BET adsorption isotherm of synthesized GCs, respectively. Whereas Figure 2a and 2b have shown PXRD, and FTIR spectrum of CHGC and CHGCCZ, respectively. TGA–DTG plot for thermal stability have shown in Figure 2c and 2d for CHGC, and (d) CHGCCZ, respectively. After preliminary characterizations, the synthesized materials GC and CHGC/CHGCCZ are subjected to the systematic TDS and As(V) ions removal, respectively.

FTIR analysis

FTIR gives the information about the available functionality present on the synthesized GCs material and their cross-linked chitosan polymer matrix (Figure 1a). The predominant peaks present in the FTIR spectrum of GCs such as a broad peak at around 3338 cm⁻¹ indicates the presence of hydroxyl (–OH), and amine (–NH₂) functionality. A peak around and 1720 cm⁻¹ signifies the presence

of keto (-C=O) functionality. The peaks at 1175 cm⁻¹ corresponds to the C-O stretching. For chitosan based CHGCCZ composites (Figure 2b), FTIR peak at 3133 cm⁻¹ confirms the presence of –OH and – N-H stretching vibrations. Whereas, the observed peaks at 1400 cm⁻¹ and 1631 cm⁻¹ support the presence of the asymmetric –N-H bending and in-plane –C-O-H bending respectively. The peaks at 1119 cm⁻¹ and 1192 cm⁻¹ corresponds to the C-O-C bond and C-O stretching, respectively. Peak at 1119 cm⁻¹ in CHGCCZ is shifted to 1113 cm⁻¹ in CHGCCZ-As.^[54] Transmittance of peaks decreases after arsenic adsorption on CHGCCZ.^[55] But in case of CHGC, transmittance of peak increases upon arsenic adsorption on to the sample.

Powder X-ray diffraction (PXRD) analysis

PXRD measurements were performed on synthesized GC material, cross-linked doped chitosan and doped chitosan-GC composite material before and after arsenic adsorption studies. GC have shown broad peaks at $2\theta = 10^{\circ}$, and 21.2° which corresponds to predominant amorphous nature of the material (Figure 1b). Now, upon mixing the GCs with chitosan for forming cross-linked matrix in presence and absence of metal oxides, we have observed new peaks along with peaks corresponding to the GCs. When CHGC and CHGCCZ cryogel were formed due to ionic crosslinking, introduction of Cu⁺² might induce the structural change in terms of specific pattern as the transition happened from non-porous oriented fibres to multilayered structure with number of voids compared to CHGC. The observed structural changes in the cryogel are also reflected in the PXRD measurements (Figure 2a). The PXRD profiles have shown characteristic diffraction patterns at $2\theta =$ 10°, 20° with other two peaks at 35° and 40° for CH and CHGC. [56] The observed diffraction patterns at 10° have diminished in CHGCCZ due to the destruction of hydrogen bonds as the introduction of Cu⁺² and Zn⁺² induces chelation in the cross-linked network. On further note, intensity of the peaks has increased significantly at $2\theta = 20^{\circ}$ which indicates higher crystallinity in metal ions doped cryogel.^[57] Again, after arsenic adsorption, the subjected cryogel have shown further increase in intensity of XRD diffraction peaks which can be attributed to the enhanced crystallinity of the crosslinked material due to the adsorbed arsenic entities. This enhanced crystallinity after As(V) incorporation into matrix would eventually decrease the accessibility of metal ions to the adsorption sites. [58] Therefore, the subjected CHGCCZ matrix had to be regenerated for test recyclability. A point to be noted is that the residual crystallinity of the composite material is the main factor which controls the accessibility of studied metal ions to the respective adsorption sites.

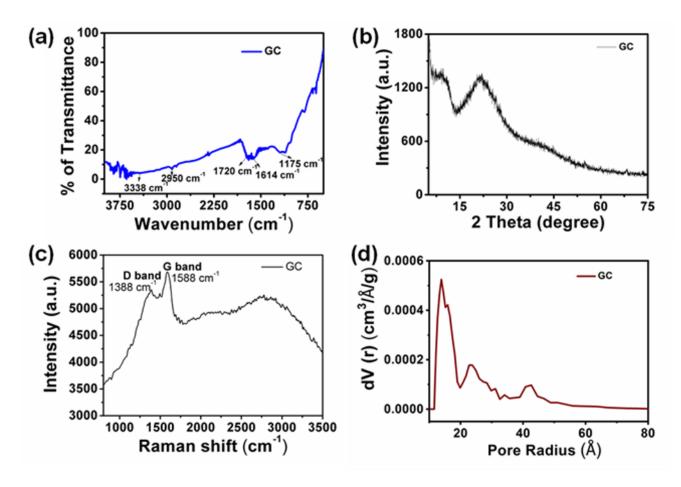


Figure 1. (a) FTIR spectrum, (b) PXRD pattern, (c) Raman spectrum, and (d) Pore volume Vs radius plot obtained from BET adsorption isotherm of synthesized GCs.

Raman analysis

The synthesized GC materials have been further charecterized by Raman spectroscopy. The obtained Raman spectrum has shown peaks at around 1388 cm⁻¹ (D band) and 1588 cm⁻¹ (G band) (Figure 1c). The peaks are quite similar to that of other avaliable activated carbon materials from other resources.^[59]

Nitrogen (N₂) adsorption isotherm

BET adsorption isotherm has shown the presence of nano pores in our synthesized GC materials upon treatment of grass samples. The pores have size distributed in the range of 10 to 50 Å (Figure 1d). Adsorption isotherm plot of adsorbed volume as a function of relative pressure according to BET model is given in the Supplementary information file (Figure S2).

Thermogravimetric analysis

Thermal stabilities of CHGC and CHGCCZ were examined by Thermogravimetric analysis (TGA) (Figure 2). For CHGC, the initial weight loss which corresponded to nearly about 6% weight loss of the material was observed at 55 °C (Figure 2c). This might be due to the slow release of trapped moisture in the studied polymeric matrix due to the presence of hydrophilic groups, *viz.*, hydroxyl and amino functionalities. The second stage of weight loss was observed to start at 180 °C.

This can be attributed to the decomposition of the chitosan and GC functionalities. At temperature of around 253 °C, the cryogel matrix was found to decompose gradually owing to the gradual destruction of primary backbone of the chitosan and GC structure. For CHGCCZ, TGA plot have shown approximately similar decomposition characteristics much like CHGC (Figure 2d). Therefore, we can conclude that both the CHGC and CHGCCZ composite materials posses sufficient thermal stability for the removal of As(V) even at elevated temperature. A point to be noted is that the TGA curve of the chitosan-based composites has shown no significant weight loss corresponding to the CuO or ZnO incorporation in the composite structure.

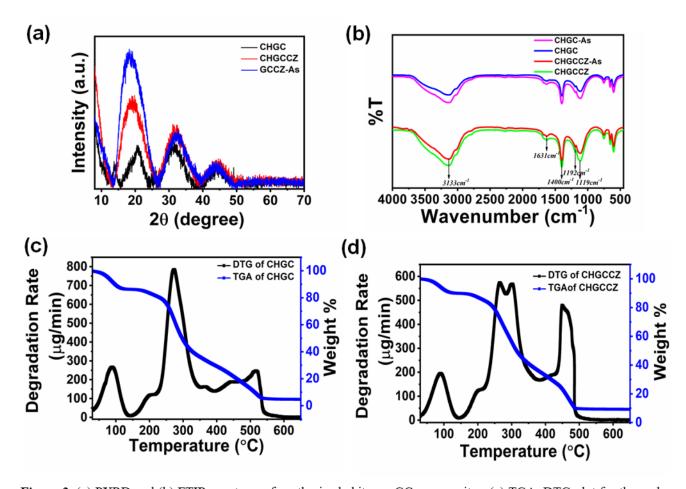


Figure 2. (a) PXRD and (b) FTIR spectrum of synthesized chitosan-GCs composites, (c) TGA-DTG plot for thermal stability for CHGC, and (d) CHGCCZ, respectively.

SEM analysis

The morphological studies of synthesized GCs and chitosan composites have been carried out using SEM and FESEM measurements. The obtained GCs are multi-layered flat flakes (Figure S1). In case of CHGC, and CHGCCZ FESEM measurements were carried out before and after As(V) adsorption process (Figure 3). CHGC has shown lesser voids or pores with lateral polymeric shrinking than CuO/ZnO doped chitosan hydrogel (CHGCCZ) which have shown large number of interconnecting large pores with multilayer formation that provided active sites for arsenic adsorption. Approximately, 50% area of the composite material is with pores. Generation of pores could be attributed to the interaction of CH with Cu⁺² metal ions on molecular level as metal ions are bonded through free amine groups (-NH₂) and C₃-hydroxyl groups (-OH) present on chitosan network. These

metal ions can induce structural changes in in-situ prepared chitosan gel which is clearly evident in morphological measurements by SEM. On further note, due to strong affinity of CH polymers toward Cu⁺² through ionic cross-linking effect, volume shrinkage in polymeric zone occurs at gel-sol interface. This phenomenon eventually leads to the structural changes from fibres to multi-layered fibrous structure with resultant number of voids.^[50] Again, after As(V) adsorption study, number of voids have been reduced significantly in the studied chitosan cryogel matrix such as CHGC-As and CHGCCZ-As (Figure 3) and the morphological study have shown similar fibrous structure like pure CHGC cryogel except induced kinkiness in the structure. This can be attributed to the efficient As(V) adsorption at available empty pores or voids in the cryogel.

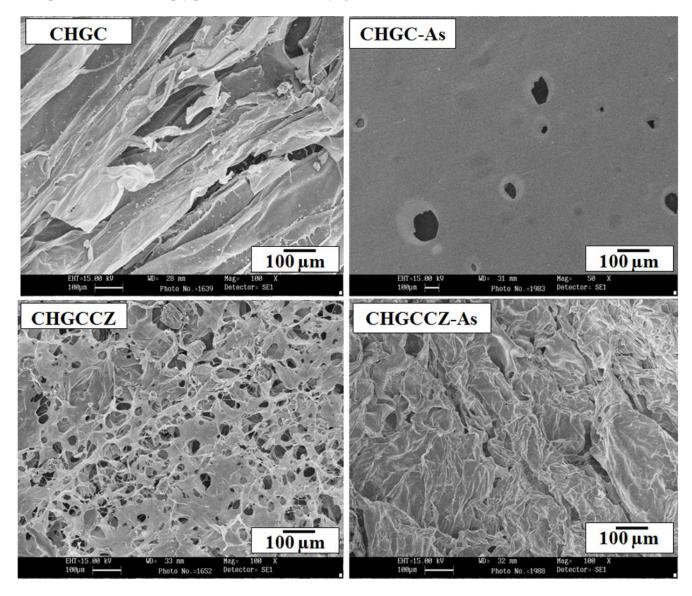


Figure 3. FESEM images of CHGC, CHGC-As, CHGCCZ, and CHGCCZ-As. The images after As(V) adsorption have shown decrease in porosity.

TDS removal studies

The water samples were collected from the local premises and were subjected to analysis for total dissolved solids (TDS) before and after treatment with GCs prepared from bermuda grass samples. TDS measured for untreated water was found to be 414 ppm. The test water for TDS measurements was allowed to pass through the GC packed in a column and TDS measurements have shown minimum decrease upto 103 ppb which is remarkable in nature (Average decrease in TDS = \sim 119 \pm 15) (Table 1). So, it is clear that GCs were effective in reducing sufficient amount of TDS and can act as TDS control material in water filtration assemblies. We have performed the TDS control studies with the same sample water using GCs in Buchner filter funnel having glass fritted disc without cotton in order to see the role of cotton in TDS removal (Figure S4). The obtained results ruled out the effects of cotton in this regard (Table T1).

Table 1. Sorption, and removal (%) of TDS (GC in a syringe and cotton)						
Amount of	TDS before	TDS after	Flow rate	Volume of	Temperature	Removal
adsorbent	filtration	filtration	(mL/min)	raw water	(°C)	%
	(ppm)	(ppm)		used (mL)		
1 g (Expt. No 1)	414	140	1.54	50	25	66.18
1 g (Expt. No 2)	414	103	1.54	50	25	75.12
1 g (Expt. No 3)	414	114	1.42	50	25	72.46
1 g (Average)	414	119 ± 15	1.50 ±	50	25	71.25
			0.05			

ICP-OES studies for Arsenic ion removal

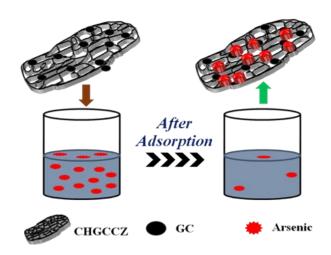


Figure 4. Schematic diagram of Arsenic ion (As(V)) removal process.

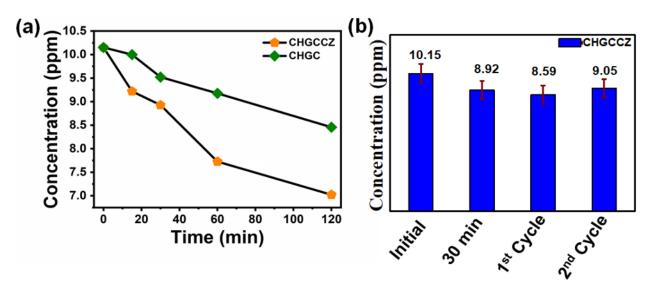


Figure 5. (a) Arsenic ions (As(V)) removal, and (b) Regeneration studies for the measurement of efficacy of CHGCCZ.

To measure the change in the concentration of As(V) in studied standard As(V) solution, adsorbents were dipped into the standard solutions for the adsorption of As(V) followed by removal of adsorbent after certain time (Figure 4) and the remaining effluents were subjected to ICP-OES measurements for the time dependent study (Figure 5a). Figure 5b represents the regeneration efficacy of CHGCCZ adsorbents. The experimental conditions associated with sorption of As(V) by the studied adsorbents are reported in the tabular form in the supporting information (Table T2). The ICP-

OES study have shown low amount of As(V) adsorption by CHGC even after 2 h duration of adsorbent dipping as the As(V) concentration was lowered down from initial 10.15 ppm to merely 9.99 ppm after 15 minutes and eventually to 8.45 ppm after 120 minutes (Figure 5a). The result indicates that adsorption of As(V) by CHGC composite material was not efficient and the CHGC was found to be degraded after 2 h of dipping. A point to remember here is that the initial As(V) was very high as compared to the available naturally contaminated solutions and the amount of adsorbent taken was very low. On the other hand, CHGCCZ have shown significant adsorption, the As(V) concentration was gradually reduced with increased time of adsorbent dipping in the studied solutions. The concentration was initially lowered down to 9.22 ppm after 15 minutes and 7 ppm after 2 h as compared to 8.45 ppm for CHGC and the subjected adsorbent matrix was still stable enough to carry out the adsorption study for longer time. This enhanced adsorption performance and stability of the CHGCCZ could be attributed to the influence of the incorporation of mainly CuO along with ZnO which have induced the enhancement of the available adsorption sites for As(V) by means of polymeric volume shrinkage which in turn increased the surface area as well as facilitated As(V) adsorption by the surface complexation process at the metal oxide adsorption surface. On further note, the plausible chemical structures involved in the adsorption of As(V) in the CHGCCZ polymeric structures are shown in the Figure 6. [60] The interaction between the arsenate ions (H₂AsO₄⁻ ions) and CHGCCZ is proposed to be via electrostatic attraction for charged species and Van der Waals attraction for neutral species. The plausible removal mechanism of arsenate ions from the aqueous phase might be due to the adsorption of arsenate ions to the protonated amine group on chitosan as expressed by:

In case of arsenate, electrostatic interaction plays a major role. The lower δ + on As and δ - on O in arsenate prefer the type II complex as electrons and charges are distributed over the two chitosan monomer moieties.

It is to be noted here that CuO is known to trigger the transformation of As(III) to As(V) and also to form Cu_3AsO_4 with As(V) which precipitates out at the metal surface and then could be adsorbed inside the adsorbent matrix. [61] Therefore, CuO seems to play a pivotal role in reducing the As(V) concentration in the subjected arsenic solution and our insightful, and systematic investigation introduces an important adsorbent material for As(V) removal from aqueous medium.

Regeneration studies were performed as it would enhance the economic feasibility and it would help to determine the reusability and efficacy of the CuO-ZnO doped chitosan-GC adsorbent composite (Figure 5b). Among the several available methods we have used acetone as regenerating solvent and in order to regenerate the used adsorbent composite material, it was dipped into acetone for ~30 min followed by washing with DI water and then drying at 100 °C for 4 h. The regenerated adsorbent was then subjected to As(V) removal study by means of adsorption process. The regeneration process was performed for few times with same adsorbent material (Table T3). We have also shown photographs to show the apparent stability of the adsorbents (Figure S3). It is noteworthy to mention that the calculated degree of swelling is found to be 112.5% after 1st cycle.

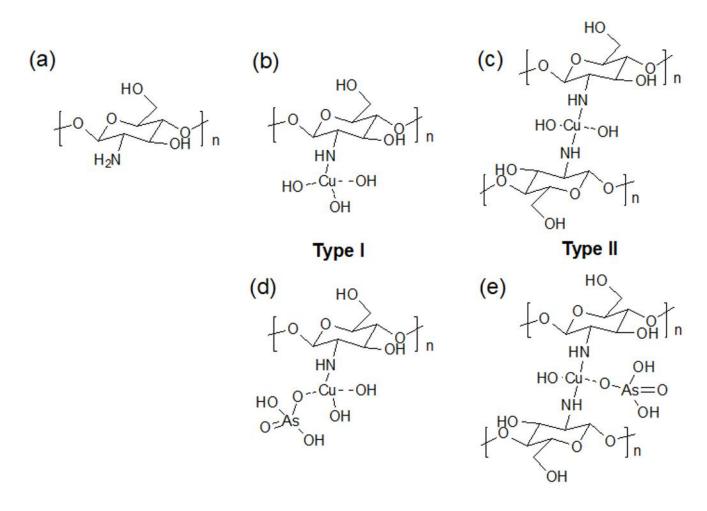


Figure 6. (a) Structure of chitosan polymer. Proposed binding structure for CuO on chitosan (b) Type I and c) Type II. Binding of As(V) on Cu-Chitosan complex (d) Type I and (e) Type II.

Adsorption studies

In order to measure the adsorption efficiency, time-dependent batch adsorption of As(V) ions onto the studied CHGCCZ adsorbent has been performed (Figure 7a). It has been observed that initial adsorption of ions which is rapid owing to their fast adsorption onto the adsorbent surface, $^{[62,63]}$ becomes sluggish due to the slow diffusion inside the pores and therefore reaches equilibrium. $^{[45]}$

The adsorption kinetics onto the adsorbent surface follows pseudo-second order rate equation,

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{1}$$

Where, K_2 (g mg⁻¹ min⁻¹), q_e (mg g⁻¹) and q_t (mg g⁻¹) denotes the rate constant, the equilibrium adsorption capacity and amount of adsorbed ions onto the surface at a particular time t, respectively. The value of K_2 can be found from the slope of the graph between t/q_t vs t (Figure 7b) and was estimated to be 0.56 g mg⁻¹ min⁻¹ and the value of q_e is estimated to be 1.14 mg g⁻¹ from the intercept of the graph.

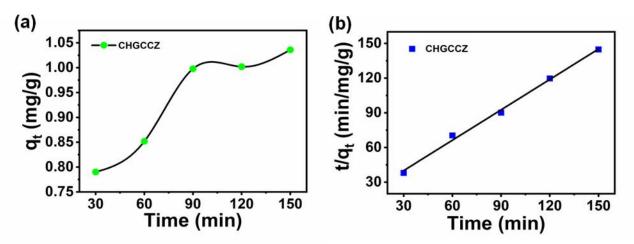


Figure 7. (a) Effect of time on the adsorption of As(V) onto the CHGCCZ adsorbent, (b) Pseudo second order kinetic model fitting of As(V) adsorption by CHGCCZ

Langmuir and Freundlich isotherm models have been employed to find out the maximum adsorption capacity of CHGCCZ adsorbent and the adsorption type. Adsorption on a homogenous and heterogenous surface is usually described on the basis of Langmuir and Freundlich isotherm models, respectively.^[64] The equation for Langmuir isotherm model is given below ^[65]

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (2)$$

Where, K_L (mL mg⁻¹) and q_m (mg/gm) denotes the Langmuir adsorption equilibrium constant and maximum adsorption capacity respectively. Dimensionless constant, R_L (from equation number 3) which is also known as separation factor, usually governs the favourability of the adsorption system.

$$R_L = \frac{1}{(1 + C_0 K_L)} \tag{3}$$

where C_0 is the highest concentration (mg/L) of As(V). Depending on the value of R_L , the type of the isotherm is determined. The isotherm is unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0 < R_L < 1$ and irreversible if $R_L = 0$. The value of R_L was found to be 0.7486 and this confirmed the favourability of Langmuir isotherm for adsorption of As(V) onto the adsorbent.

Our experimental data fits reasonably well into Langmuir isotherm model with obtained correlation coefficient value (R^2) ~0.96. The adsorption isotherm of As(V) on CHGCCZ adsorbent is represented in Figure 8a. It demonstrates that the maximum uptake of As(V) on CHGCCZ was 0.626 mg g⁻¹. The Langmuir adsorption graph is obtained by plotting C_e/q_e against C_e (Figure 8b). The K_L , obtained from the intercept, is found to be ~0.23 L mg⁻¹. The estimated value of q_m from the slope of the graph is ~555.55 mg/g.

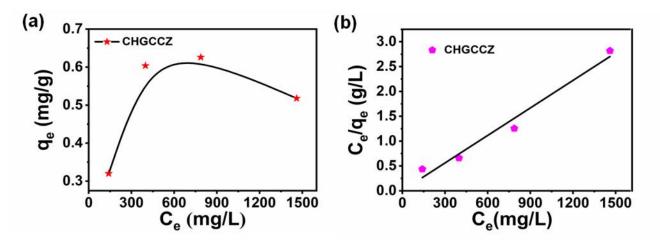


Figure 8. (a) Adsorption isotherm, and (b) Langmuir isotherm model for As(V) adsorption onto CHGCCZ adsorbent.

Conclusion

In summary, we report a simple, cost-effective and viable solution for the effective removal of TDS and arsenic ions by utilization of bio-composite materials. The present study explicitly demonstrates that adsorption using chitosan composites is becoming a promising alternative to replace conventional adsorbents in removing toxic arsenic ions. CuO doped chitosan and GC based composite material, CHGCCZ adsorbent have been found to be quite efficient, stable and reusable for the adsorption of As(V). The adsorption mechanism of chitosan based CHGCCZ composites is interesting as it has shown dependency on its cationic nature and our studied composites is proposed to have interacted with the metal anions through anion exchange/electrostatic attractions and chelation. It has been found that after adsorption for 2 h, the concentration of As(V) in the effluent was significantly reduced by 31% (7.02 ppm from 10.15 ppm). The recyclability of the adsorbent was found to be quite satisfactory up to 2 cycles when the regeneration process was carried out using acetone. Recyclability and efficacy of the adsorbent material for removal of arsenic from drinking water can further be improved through careful and systematic investigation of adsorption kinetics and its' mechanism.

Acknowledgement

MKC acknowledges IIT Roorkee for Institute Post-Doctoral Fellowship. SS like to acknowledge DST Water Technology Initiative Grant (No. DST/TM/WTI/2K16/50(G). AB thanks Department of Science and Technology-Science and Engineering Research Board (DST-SERB) grant YSS/2015/001042 for funding and BML Munjal University for Professional Development Allowance.

Conflict of Interest

The authors declare no conflict of interest.

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Table of Content

Inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements have been performed to study the arsenic ion (As(V)) adsorption efficacy of the prepared porous cross-linked adsorbent materials (CHGCCZ) made of metal oxides doped bio-compatible chitosan polymer and nano porous carbon material (GC) which is derived from naturally available Bermuda grasses. GCs have also been employed for the removal of total dissolved solids (TDS) from aqueous medium.

