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ORIGINAL ARTICLE

Ceria modified activated carbon: an efficient arsenic removal adsorbent for drinking water purification

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Abstract Ceria (CeO_2) coated powdered activated carbon was synthesized by a single step chemical process and demonstrated to be a highly efficient adsorbent for the removal of both As(III) and As(V) from water without any pre-oxidation process. The formation of CeO_2 on the surface of powdered activated carbon was confirmed by X-ray diffraction, Raman spectroscopy and X-ray photoelectron spectroscopy. The percentage of Ce in the adsorbent was confirmed to be 3.5 % by ICP-OES. The maximum removal capacity for As(III) and As(V) was found to be 10.3 and 12.2 mg/g, respectively. These values are comparable to most of the commercially available adsorbents. 80 % of the removal process was completed within 15 min of contact time in a batch process. More than 95 % removal of both As(III) and As(V) was achieved within an hour. The efficiency of removal was not affected by change in pH (5–9), salinity, hardness, organic (1–4 ppm of humic acid) and inorganic anions (sulphate, nitrate, chloride, bicarbonate and fluoride) excluding phosphate. Presence of 100 ppm phosphate reduced the removal significantly from 90 to 18 %. The equilibrium adsorption pattern of both As(III) and As(V) fitted well with the Freundlich model with R^2 values 0.99 and 0.97, respectively. The material shows reusability greater than three times in a batch process (arsenic concentration reduced below 10 ppb from 330 ppb) and a life of at least 100 L in a column study with 80 g material when tested under natural hard water (TDS 1000 ppm, pH 7.8, hardness 600 ppm as $CaCO_3$) spiked with 330 ppb of arsenic.

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Introduction

Occurrence of dissolved arsenic species in drinking water and its health consequences has been a serious concern throughout the world. Several geographies across the world are affected by the presence of high concentration of arsenic in drinking water (Chen et al. 1994; Karim 2000; Zhang et al. 2010). Millions of people are at the risk of chronic arsenic poisoning in Bangladesh and India. It has been estimated that an approximate of 35–77 million people in Bangladesh are at the risk of drinking arsenic contaminated water (Ahmad et al. 1997; Chowdhury et al. 1999; Maji et al. 2008; Argos et al. 2010). Due to high health risks associated with the consumption of arsenic contaminated water and food products, the World Health Organization (WHO), European Union, and the US Environmental Protection Agency (US EPA) have set the arsenic standard for drinking water as 10 µg/L (10 ppb) to protect consumers from the long time chronic exposure to arsenic (Sabbatini et al. 2010).

Several methodologies for arsenic removal from drinking water have been reported. These include coagulation/filtration, ion-exchange, membrane technologies, chemical precipitation and adsorption (Bordoloi et al. 2013; Wickramasinghe et al. 2004; Nguyen et al. 2009; Mohan and Pittman 2007). Adsorption process is generally considered to be more attractive compared to other technologies due to ease of use and low cost (Mohan and Pittman 2007; Ali 2010, 2012). Many low cost adsorbents, e.g., iron and iron oxide based compounds, activated alumina, hydrotalcites, rare earth oxides, flyash (Zhang et al. 2003; Xu et al. 2013; Li et al. 2010; Ali et al. 2012, 2014),

and bio sorbents have been used for arsenic removal. However, most of the studies have been reported on very fine sized adsorbent particles that would require further processing like granulation, etc., before they could be used either in community scale purification systems or point of use (POU) devices to reduce immediate caking and chocking of filters. Also many adsorbents require frequent consumer intervention like pre-oxidation, pH adjustment and regular regeneration process. Furthermore, use of very fine particles could lead to possible release of nanomaterials into the environment that is currently becoming an issue of concern (Cui et al. 2012). Hence development of adsorbents that are highly efficient, low cost, require minimal consumer intervention when used and do not pose threat to the environment is a need of time.

Cerium dioxide is a widely used chemically stable and nontoxic rare earth oxide which makes it a strong candidate for water purification. Cerium di oxide has been shown to have strong affinity towards arsenic and have removal capacity more than 100 mg/g when used as hydrous cerium oxide (Li et al. 2012). But as stated above, the studies have been reported for nanosized particles that would require granulation before any practical applications. Granulation could lead to reduced removal capacity due to drastic change in available surface area.

Herein we have reported an efficient arsenic removal adsorbent that could directly be used in a loose bed or bound block for POU device or in community scale purification. The adsorbent consists of powdered activated carbon modified with in situ synthesized ceria particles. With equal efficiency of removal for both As(III) and As(V) without any pre oxidation, the material could be well competitive in terms of cost, ease of use and removal efficiency in comparison to any other commercially available adsorbents for arsenic removal.

Materials and methods

Materials used

Powdered activated carbon (PAC) was purchased from HAYCARB Sri Lanka. The source of activated carbon is coconut shell as mentioned by the supplier. Cerium Nitrate, Sodium Hydroxide and Hydrochloric acid were purchased from Merck Chemicals, India, and were of laboratory reagent grade. All the chemicals were used as received without any further purification or treatment.

Characterization techniques

X-ray diffraction (XRD) spectra of the samples were collected using Siemens D 5000 at a step rate of 0.5 degree

two theta. Zeta potential of the samples were determined using ZETA POTENTIAL METER, MFGPRO-52400035. ICP-MS measurements were carried out using a Perkin Elmer Optima 2000 DV instrument. BET surface measurements were done using SMARTSORB-92 of Smart Instruments. X-ray photoelectron spectra (XPS) were recorded using Model ESCA+ by Omicron UK using a Al k alpha source. Raman spectra were recorded using Renishaw Invia Raman microscope powered by a laser source @ 785 nm. ICP-MS studies were carried out with an Agilent-7700 ICP-MS instrument using EPA method 200.8. FTIR spectra were collected in a PERKIN ELMER SPECTRUM ONE instrument with diffuse reflectance sampling accessory.

Experimental procedures

Synthesis of PAC–CeO$_2$

100 g of powdered activated carbon was added to 80 mL of 0.071 M Cerium Nitrate (Ce(NO$_3$)$_3$·6H$_2$O) solution and left undisturbed for 3 h. 1 N NaOH solution was then added drop wise to the above mixture with continuous mechanical stirring to obtain a pH value of 6.5. The mixture was then filtered, washed and dried at 100 °C to yield the final material PAC–CeO$_2$.

Adsorption isotherm

0.1 g of PAC–CeO$_2$ was added to 100 mL of 300 ppb As(III) or As(V) solution and agitated for 4 h. The solution was then allowed to equilibrate for 72 h. 20 mL aliquots were collected after 72 h, filtered through a 0.45 μm syringe filter and used for arsenic estimation.

Equilibrium studies were carried out at different input concentrations of arsenic. Based on the equilibrium arsenic concentrations, an adsorption isotherm was plotted. Arsenic concentrations in the aliquots were estimated using ICP-OES.

Kinetics studies

1 g of PAC–CeO$_2$ was added to 1 L of 300 ppb As(III) or As(V) solution. 20 mL aliquots were collected at 2, 4, 6, 8 and 10 min. Further aliquots were collected at 15, 30, 60 and 90 min. The aliquots were filtered through a 0.45 μm syringe filter and clear filtrate was used for arsenic estimation.

Effect of pH on removal capacity

pH of 300 ppb As(III) or As(V) solution was adjusted to the required value using 0.1 N HCl and/or 0.1 N NaOH

solution. 0.1 g of PAC–CeO$_2$ was then added to 100 mL of As(III) or As(V) solution, agitated for 4 h and then allowed to equilibrate for 72 h. Aliquots were collected after 72 h, filtered through a 0.45 μm syringe filter and used for arsenic estimation.

Effect of counter-ions and organics on removal capacity

Effect of counter-ions was studied using 300 ppb As(III) or As(V) solution spiked with 100 ppm of the counter anion. The studies were carried out with single counter anion. For studies involving organics, 300 ppb As(III) or As(V) solution was spiked with 1–4 ppm of humic acid. Equilibration and sample collection were done using identical procedure as pH studies.

Reusability study

0.1 g of PAC–CeO$_2$ was added to 100 mL of 330 ppb As(III) or As(V) solution agitated for 4 h. The solution was then allowed to equilibrate for 72 h. 20 mL aliquots were collected after 72 h, filtered through a 0.45 μm syringe filter and used for arsenic estimation. The adsorbent was then filtered, washed with DI water and dried at RT before repeating the experiment.

Column study

80 g of the adsorbent was filled in a column of 15 cm long acrylic column with a diameter 3 cm to get a packed bed. Both ends of the column were covered with fine metal mesh and porous Nylon membrane to prevent the material from flowing out. The test water [Natural water with, TDS 1000 ppm, pH 7.8, hardness 600 ppm as CaCO$_3$ and spiked with 330 ppb As(III) and As(V)] was passed continuously through the column in one direction (from top to bottom) using a peristaltic pump at 50 mL/min and the output water was tested for its arsenic content at 5, 50, 100 and 150 L. The tests were discontinued as soon as the output arsenic concentration was measured beyond 10 ppb.

Results

Adsorbent characterization

XRD pattern of the adsorbent confirmed the formation of CeO$_2$ on the surface of PAC. The d values could be indexed to face-centered cubic phase of CeO$_2$ (JCPDS card No. 34-0394). No other impurities were detected, which indicated high purity of the sample. Figure 1 shows the XRD patterns of the as synthesized adsorbent as well as
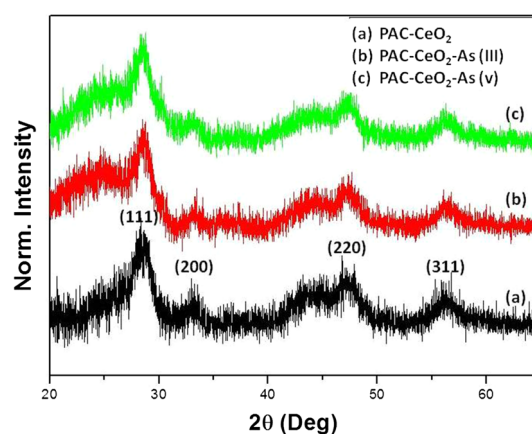

Fig. 1 XRD patterns of PAC–CeO$_2$ before and after treatment with As. The *peaks* are indexed to face centered cubic phase CeO$_2$

after the Arsenic adsorption studies. No noticeable change was observed indicating the Arsenic adsorption process to be completely a surface phenomenon.

The amount of CeO$_2$ deposited (as Ce) has been quantified using ICP-OES which shows the presence of 3.5 % cerium. The BET surface area of PAC decreases from initial value of 1050–635 m^2/g after CeO$_2$ deposition confirming the presence of surface deposits.

Presence of Raman shift at 461 cm^{-1} (Fig. 2a inset) confirmed the formation of CeO$_2$ (Saitzek et al. 2008). The Raman shifts at ∼1300 and 1589 cm^{-1} are due to the G and D band of powdered activated carbon (Shimodaira and Masui 2002). Due to the strong intensity of the Raman shifts of carbon, the CeO$_2$ peaks are shown in the inset of Fig. 2a. Figure 2a also shows the Raman shifts of the PAC–CeO$_2$ system after the arsenic adsorption studies. No change in the Raman shift had been observed which further confirmed the role of only surface phenomena in the adsorption process.

XPS spectra (Fig. 2b) for the adsorbent show the presence of Ce in it. This conforms to the Ce 3d$_{5/2}$ features at 882.37, 887.86, and 898 eV and Ce 3d$_{3/2}$ features at 900.82, 907.53, and 916.4 eV as reported in the literature (Cheng et al. 2008). The main peaks at 882.37 and 900.82 represent the 3d^{10} 4f^0 initial electronic state corresponding to the Ce^{4+} ion, while the absence of any peak at 884.9 eV rules out the presence of any Ce^{3+} ions in the adsorbent.

Change of zeta potential value of PAC from −50 to +62 mV also confirmed the surface modification of the PAC surface.

Adsorption isotherm

The adsorption isotherm (Fig. 3a, b) was determined from equilibrium studies carried out at different As(III) and As(V) concentrations. The adsorption isotherm was plotted
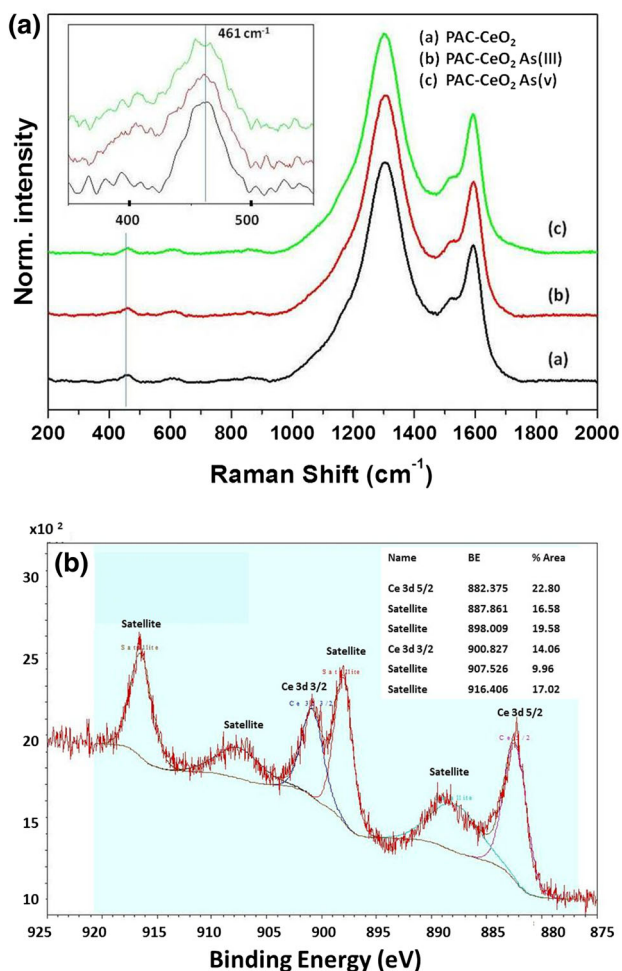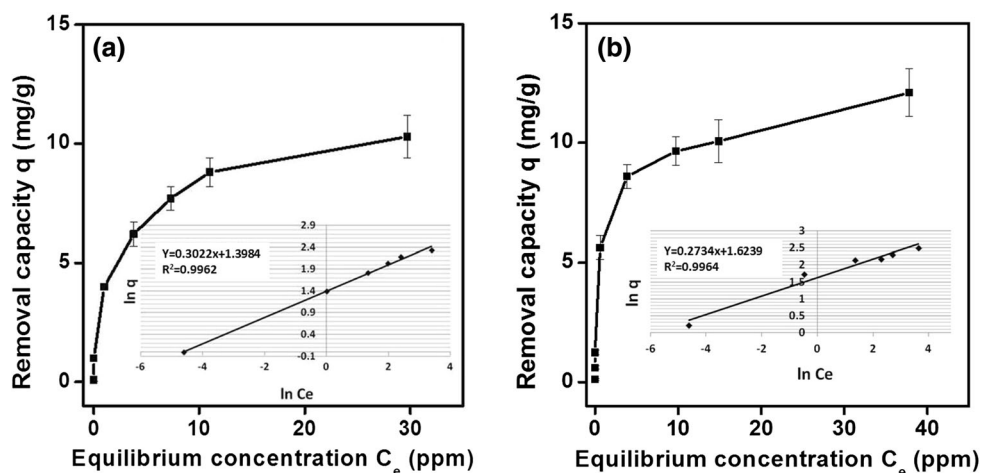
Fig. 2 **a** Raman shifts of PAC–CeO$_2$ before and after treatment with As, and **b** XPS spectrum of PAC–CeO$_2$

taking removal capacity q (mg of As/g of adsorbent) on the Y axis against equilibrium concentration C_e (ppm) of As(III) or As(V) on the X axis. The plots show best fit for

Freundlich adsorption isotherm (inset) with values $n = 3.3$, $k = 0.714$ and $R^2 = 0.9962$ for As(III) and $n = 3.7$, $k = 0.625$ and $R^2 = 0.964$ for As(V).

Kinetics

The kinetics of As(III) and As(V) removal was studied at 300 ppb initial concentration with a adsorbent loading of 0.1 g/L. 80 % of the adsorption was completed within first 15 min of contact for both As(III) and As(V) (Fig. 4a). This showed the effective use of PAC–CeO$_2$ adsorbent for the removal of both As(III) and As(V) without any pre-oxidation process. The experimental results could be best fitted with a pseudo-second-order rate kinetic model as demonstrated in Fig. 4b and c. The effectiveness of the model could be justified from the R^2 values nearing 1 (Fig. 4b, c).

When the base material PAC was used as an adsorbent under the same conditions for comparison purpose, the maximum removal obtained was 10 % even after 90 min. The maximum removal capacity at equilibrium concentration of 40 ppm was found to be 0.83 mg/g.

Effect of pH

Since pH of water could alter the surface charge of the adsorbent/adsorbate and hence influence the kinetics and removal capacity of most of the adsorbents, Arsenic removal studies were carried out at different pH (5, 6, 7, 8, 9) of the input water at same arsenic concentration of 300 ppb (Fig. 5). No significant change in the removal capacity in different pH values in case of As(III) was observed although maximum removal was observed at pH 6. This could be explained on the basis of variation in arsenic species depending on pH values. As(III) exists predominantly as H$_3$AsO$_3$ below pH 9.2 and as H$_2$AsO$_3^-$

Fig. 3 Adsorption isotherm of **a** As(III) and **b** As(V) on PAC–CeO$_2$. Inset show the Freundlich adsorption isotherms

Fig. 4 a Kinetics of adsorption for As(III) and As(V) on PAC–CeO$_2$. **b, c** The pseudo second order rate kinetics of the adsorption process
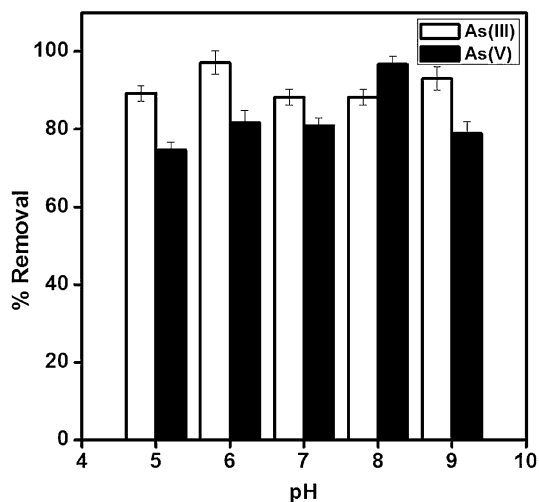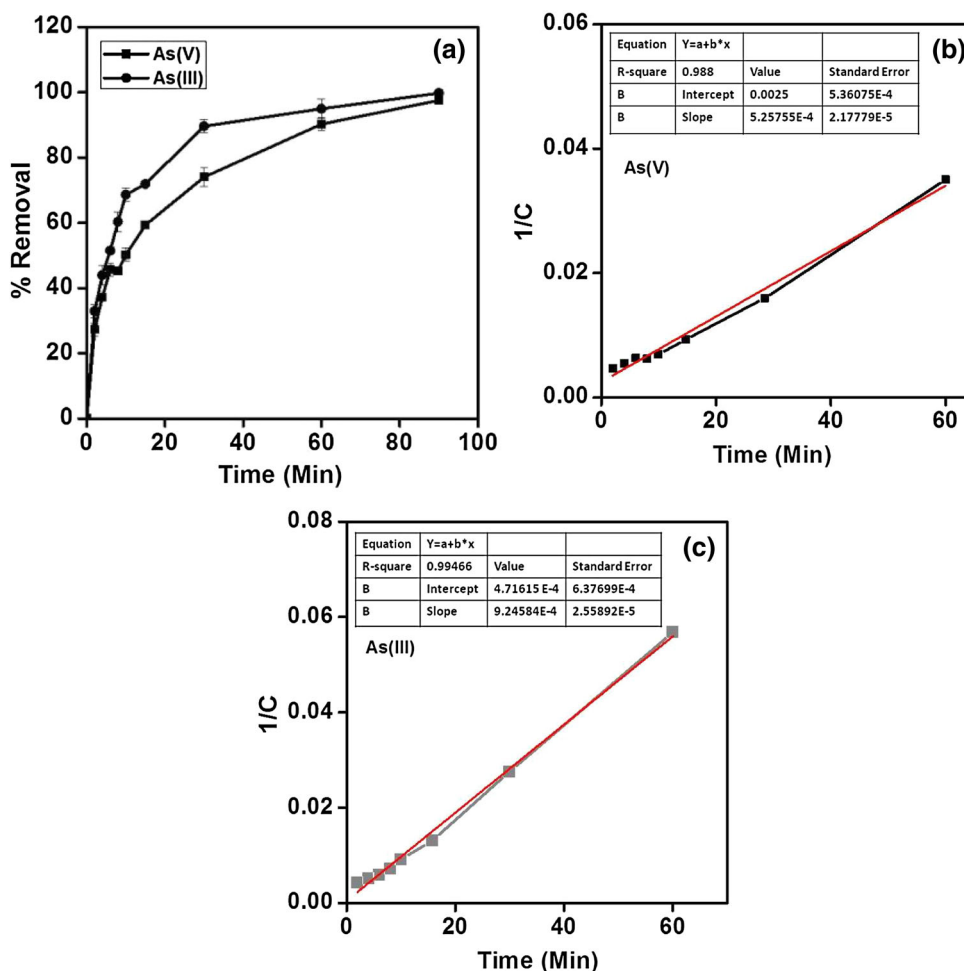

removal. The As(III) adsorption onto PAC–CeO$_2$ was not affected by the increase of solution pH, which suggests strong affinity existing between As(III) anions and the CeO$_2$ particles in PAC–CeO$_2$. Thus, PAC–CeO$_2$ could be readily used for the removal of As(III) within a wide range of solution pH, which is beneficial to their applications for water bodies with various conditions.

For As(V) the highest removal was observed at pH 8 (Fig. 5). This observation could also be explained on the basis of As(V) speciation with respect to pH. As(V) mainly exists in its anionic forms within the pH range from 4 to 10 (H$_2$AsO$_4^-$ as the main species at pH range 3–6, HAsO$_4^{2-}$ and AsO$_4^{3-}$ as major species at pH 8) (Deng et al. 2010). The more negative nature of the arsenic species facilitates the higher adsorption on the positively charged adsorbent at pH 8 and hence the highest removal.

Effect of counter ions

To investigate the competing effect from co-existing anions in aqueous environment that could negatively effect the removal efficiency of the adsorbent, arsenic adsorption
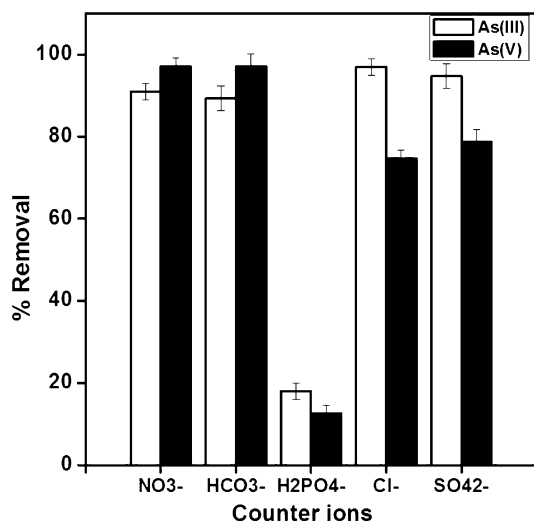

Fig. 5 Percentage removal of As(III) and As(V) by PAC–CeO$_2$ at different pH values

above 9.2. Since the pH of the experiments was below 9.2, the adsorbent did not exert any electrostatic force towards neutral H$_3$AsO$_3$ and hence no significant variation in

Fig. 6 Percentage removal of As(III) and As(V) by PAC–CeO$_2$ in presence of different counter ions

Fig. 7 Percentage removal of As(III) and As(V) by PAC–CeO$_2$ in presence of humic acid

studies were carried out separately in presence of Sulphate, Nitrate, Chloride, Bicarbonate and Phosphate (Fig. 6). The concentration of the counter anions were maintained at 100 ppm. Even at this high concentration, presence of chloride, nitrate, sulphate and bicarbonate had negligible effect on As(III) removal. However, in the presence of 100 ppm sodium dihydrogen phosphate, the removal drops from an average of over 90–18 %. This might be explained on the basis of their similar ionic structure that could have led to competitive adsorption (Li et al. 2012). The same trend was observed in case of As(V) adsorption also. It was also observed that the percentage removal of As(V) was less compared to As(III) in presence of Cl$^-$ and SO$_4^{2-}$. This could also be explained on the basis of anionic nature of As(V) at pH of the experiment ($\sim$8) and the competing adsorption of the ions on the adsorbent surface.

Effect of humic acid

Presence of humic acid up to 4 ppm (Fig. 7) in the test water does not have any perceivable effect on the removal As(III). The removal of As(V) was reduced slightly in the presence of humic acid. The low removal of As(V) in presence of humic acid was also observed by Rao et al. (2009) with a zero valent ion (ZVI) adsorbent.

Reusability

The reusability studies of the material using a natural hard water (TDS 1000 ppm, pH 7.8, hardness 600 ppm as CaCO$_3$) spiked with 330 ppb of As(III) or As(V) revealed that the material could be used at least three times before the output concentration of As solution exceeds the limit of 10 ppb,
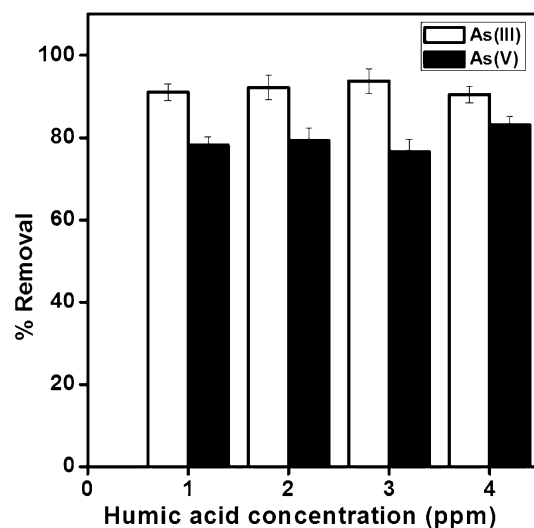
reiterating the significance of the material as an efficient adsorbent for As removal. The material could be used even up to five times under identical conditions if the output limit is put at 50 ppb (as per India and Bangladesh standards).

Column studies

Column studies were done with 80 g material in a column of 15 cm long acrylic column with a diameter of 3 cm. The flow rate was maintained at 50 ml/min using a peristaltic pump. The test water was prepared using natural hard water (TDS 1000 ppm, pH 7.8, hardness 600 ppm as CaCO$_3$). Table 1 shows the values of output As concentration measured at different time points.

Cerium leach

Absence of purification byproducts or presence below maximum contamination limit (MCL) in the output water is an important factor in determining the safe usability of any adsorbent. To determine the amount of cerium leached into the output water, ICP-OES studies were done on the output water of the batch adsorption studies. With an instrument detection limit of 50 ppb, the maximum Ce concentration in the output water was found to be below detection limit at the pH values between 6.5 and 8.5 which accounts for most of the drinking water scenario. At acidic pH and pH values beyond 9, we were able to detect Ce in the output water up to 1.1 ppm when the equilibrium concentration of As was 10 ppm. The MCL for cerium in drinking water context is not defined in US EPA or WHO guidelines till now. Hence comments could not be made about the usability of the material at pH values below 6.5 or beyond 9.

Table 1 Output concentration of As(III) and As(V) from column studies

Time point (L)	As(III) (ppb)	As(V) (ppb)
5	<1	<1
50	3	<1
100	9	7
150	23	51

Discussion

Mechanism of removal

The adsorption kinetics study is helpful to understand the mechanism of adsorption reactions. The pseudo-second-order kinetic model is based on the assumption that the rate-limiting step may be chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate which is suitable for sorptions at low initial concentration. In this case, the pseudo-second-order kinetics indicates that the arsenic adsorption on PAC–CeO$_2$ happens through chemisorption, which has also been discussed in the FTIR study (Li et al. 2012; Cui et al. 2012). This result was also supported by the X-ray diffraction and Raman studies that indicated no change into the crystal structure or surface properties of the adsorbent before and after the arsenic adsorption studies.

The mechanism of arsenic removal was further investigated using FTIR technique. To ensure quantitative analysis, samples were mixed at 1 % with KBr by weight. From the spectra it could be seen that before the arsenic adsorption (Fig. 8a), strong OH stretching and bending vibrations of surface adsorbed water at 3435 and 1629 cm^{-1} along with Ce–OH bending vibrations at 1110, 1055, 930 cm^{-1}, are present. After the arsenic adsorption experiments (Fig. 8b, c), the Ce–OH bending vibrations disappeared and a new vibration at 839 cm^{-1} appeared which could be attributed to ν(As–OCe) bond. Appearance of this vibration at 815 cm^{-1} for adsorption of arsenic onto TiO$_2$ was reported by Pena et al. (2006). Li et al. (2012) reported observation of the same peak at 805 cm^{-1}. Appearance of this As–O–Ce vibration indicates that the adsorption of both As(III) and As(V) follows the inner sphere mechanism. The FTIR studies indicate that the substitution of OH groups by As from Ce–OH plays a major role in the adsorption process which could also be explained through specific adsorption mechanism. The specific adsorption involves ligand exchange reactions where the anions displace OH$^-$ and/or H$_2$O from the surface (Hingston et al. 1967).

Since the surface charge of the PAC–CeO$_2$ adsorbent was positive in the experimental pH range, the coulombic attraction between the positive surface and negative anions also played a role in giving the adsorbent a high removal capacity for both As(III) and As(V) across pH ranges.
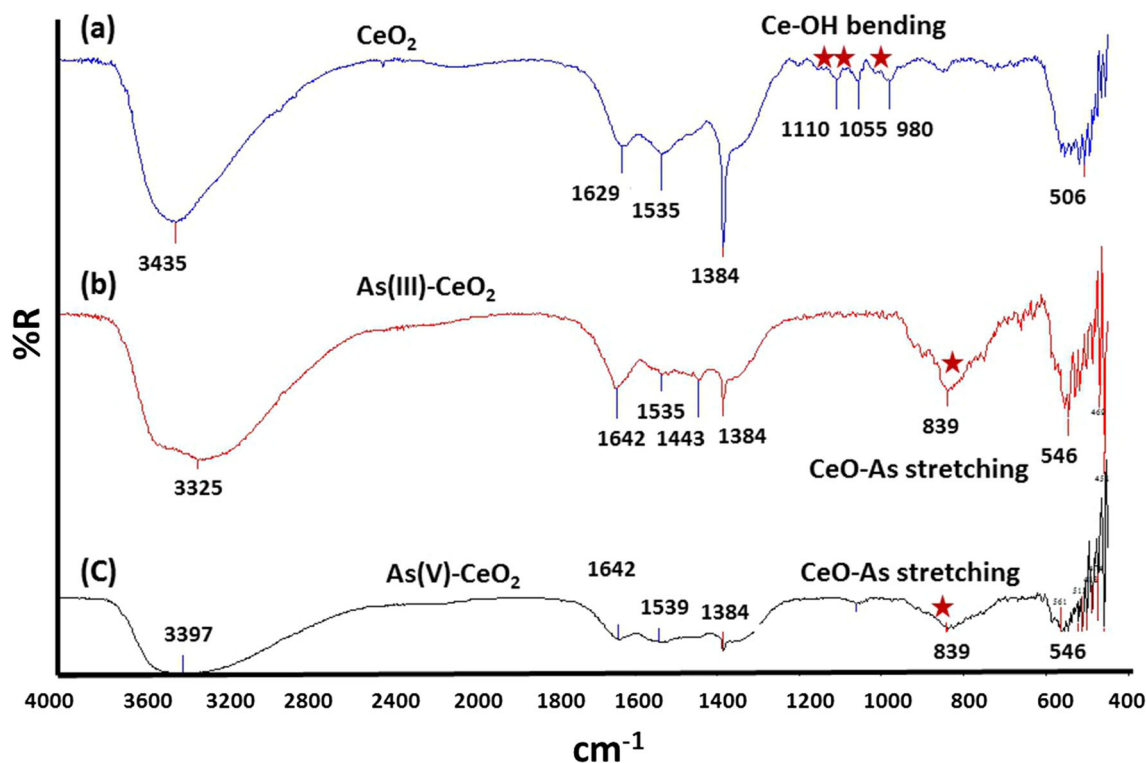

Fig. 8 FTIR spectra of PAC–CeO$_2$ **a** before and **b** after removal of As(III) and **c** after removal of As(V)

Conclusion

The CeO$_2$ coated powdered activated carbon (PAC–CeO$_2$) is highly efficient as an adsorbent for arsenic removal from drinking water. The maximum removal capacity was found to be nearly 12 mg/g for both As(III) and As(V). The efficiency of removal was not affected by change in pH, salinity, hardness, organic and inorganic anions excluding phosphate. The mechanism of removal is through both specific adsorption and columbic attraction. With no pre-treatment required, the adsorbent could be highly competitive for POU devices in terms of cost, ease of use and removal efficiency.

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