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Preparation, characterization and application studies of inorganic-organic novel polymer composite

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ABSTRACT

A novel iron doped chitosan coated activated alumna (IDCA) derivative was prepared and spectroscopic studies including FTIR, Elemental analysis (EA), XRD, and SEM were used for its characterization. Thermodynamic behavior of the adsorbent was evaluated by Thermogravimetric Analysis (TGA) and Differential Scanning calorimetry (DSC) analysis. The pore size distribution and nitrogen adsorption isotherm revealed the existence of micro porous structure. The applicability of the adsorbent towards the removal of arsenite and arsenate has been demonstrated. Copyright © 2010 VBRI press.

Keywords: Chitosan; arsenic; composite; nitrogen adsorption isotherm.

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Mohammad Yunus, *Head* of Department of Environmental Sciences, Director, USIC and *Former Dean* of School for Environmental Science, Babasaheb Bhimrao Ambedkar (A Central) University *was offered the Post of Professor in absentia* in recognition of his outstanding contributions in the area of environmental sciences. He held the positions of the *Registrar* of the University for more than one year and served as *Acting Vice-chancellor* many a times. Formerly, he was *Head* Environmental Sciences Division at Lucknow based National CSIR Lab. – The *National Botanical Research Institute*. With more than *37 years research & academic experience*, he has contributed more than *105 original research papers* (more than 60 in reputed foreign journals), and *published 6 edited books* (3 from abroad- John Wiley's, UK; Taylor & Francis, UK; Kluwer Academics, The Netherlands). His academic interest focuses on air pollution & plants, global atmospheric issues, environmental impact assessment and disaster management. He is known for the scientific concepts he evolved viz. pollution sink ability of plants and eco-auditing.

Nalini Sankararamakrishnan received her PhD from Indian Institute of Technology, Chennai, India in 1997. After a short span as visiting scientist in University of Illinois, Urbana Champaign, she joined Rutgers University, New Jersey as Post doctoral Research fellow in the department of Civil and Environmental Engineering. She then joined Indian Institute of Technology, Kanpur in 2002 as Senior Project Scientist. She is currently working as Research Scientist in Centre for Environmental Sciences and Engineering at IIT Kanpur. Her research interests include evaluation of field kits, mechanism of mobilization of arsenic, eco-friendly approach for industrial effluent treatment, defluoridation and decontamination of arsenic from ground water. Currently her group has developed a novel biopolymer for the decontamination of arsenic from arsenic contaminated drinking water.

Introduction

In present time, both the poor and developing countries face drinking water toxicity problem which directly affect the food chain and creates highly health hazardous problems in the level of mass poisoning. In respect to toxicity and notorious behaviors, the most dangerous toxins are Arsenic, Chromium, Cadmium, Fluoride, and Lead [**1-6**] in which arsenic is most serious matter of concern for developing countries. It is a matter of challenge to mitigate arsenic in large scale and community level. A wide range of treatment procedures has been reported for the removal of excess contaminants from water. These can be broadly divided into three categories: precipitation, adsorption and membrane based in which adsorption process are frequently used. Activated alumina, activated carbon, polymeric resins, chitosan beads, and few other low cost adsorbents were successfully tried for arsenic removal [**7-18**].

Activated alumina is widely used as an adsorbent for water treatment in rural as well as urban applications [**4**]. Its unique characters of physical and chemical textural properties make it better than other transitional inorganic oxides [**19**]. It is reported that coating of alumina improves both the uptake capacity and surface area [**20**]. Due to its high affinity of water pollutants, it proves as a promising adsorbent but there are few disadvantages which include clogging of bed during scale up operations, fungal and microbial growth.

During the past two decades, biosorption has received much attention due to the diversity of the available sorbent materials, such as fungal or bacterial biomass and alginate or chitosan biopolymers. In recent years, many studies have been reported on impregnation/coating/doping of various oxides, sand, carbon, polymer, spent catalyst [**21-25**] and these have been shown to be very effective for removal of toxic metals. Chitosan is a natural, cationic aminopolysaccharide copolymer of glucosamine and N-acetylglucosamine, obtained by the alkaline, partial deacetylation of chitin, which originates from shells of crustaceans such as crabs and prawns [**26**]. Chitosan is a non-toxic, hydrophilic, biodegradable, biocompatible, mucoadhesive, and anti-bacterial, biopolymer which has led to a very diverse range of its applications [**27**]. It has attracted tremendous attention as novel functional materials and potentially important renewable agricultural resource. The presence of a large number of amine groups on the chitosan chain increases the adsorption capacity of chitosan [**28-30**].

A number of studies have been carried out on the preparation, characterization and applications of new organic–inorganic hybrid polymeric composites due to its better handling properties [**31**]. Polymeric composites can be made into usable forms viz., physical modifications (beads, membranes, candles, etc.) or chemical modifications. But the use of polymeric composites for removal of toxic ions is very scanty [**32-34**].

The purpose of this work is to synthesize an organic and inorganic smart bio-composite by dispersing the alumina particle in the iron doped chitosan polymeric matrix. The material was examined for its surface morphology/topography by SEM, FT-IR and XRD. The surface area and porosity was studied by nitrogen adsorption isotherm. The thermogravimetric analysis (TGA) was carried out with its DSC, showing its endothermic reaction. The newly formed iron doped chitosan coated activated alumina (IDCA) was tested for its ability to arsenic removal from drinking water/aqueous solutions.

Experimental

Materials

Chitosan flakes was acquired from India Sea foods, Cochin, India and used without any further purification. The degree of deacetylation was reported to be 88% by the manufacturer. The details of chitosan flakes are given as: (Ash: < 1%, Moisture: < 10%, Viscosity (1%): < 100 cps, Mesh: < 0.6 mm). The two types of Activated alumina grades (DF-101 & F-101) were purchased from M/S Bhargava Alumina Industries, Surat, India. Comparing the uptake capacity of arsenic and few basic characteristics, DF-101 grade of activated alumina was found better and used in further study (**Table 1**).

Stock arsenate As(V) solution of 1000 ppm was prepared by dissolving Merck grade 0.4165 gm disodium hydrogen arsenate heptahydrate ($Na_2HAsO_4.7H_2O$), along with 5 mL 1N sulphuric acid, in 100 mL de-ionized water. Stock arsenite As(III) solution of 1000 ppm prepared by dissolving Merck grade 0.1732gm sodium arsenite ($NaAsO_2$) in 100 mL de-ionized water. All other chemicals used were of analytical grade.

Preparation of IDCA (Iron doped chitosan coated activated alumina)

Preparation of activated alumina: Composite chitosan biosorbent (IDCA) was prepared by coating activated alumina with chitosan gel. Activated alumina was dried in an oven for 6 hr at 110 – 130 °C. The dried alumina was stirred with oxalic acid for 6 hr at room temperature to coat the surface. The alumina was filtered from the acid, washed twice with DI water, and dried in an oven at 80 °C under vacuum for 24 H. About 50 g of chitosan with 2.5 g iron chloride was slowly added to 1000 mL of 10 wt % oxalic acid solution with stirring.

Preparation of chitosan coating: The acid and chitosan form a viscous mixture (gel), which must be heated to 40−50 °C to facilitate mixing [**35**]. Approximately 500 mL of the chitosan gel was diluted 2-fold with water and heated to 40−50 °C. About 500 g of the acid-treated alumina was slowly added to the diluted gel and stirred for about 36 h. The contents were allowed to settle, and the clear liquid was filtered out under vacuum with Whatman 41 filter paper. The composite biosorbent was washed twice with DI water and dried in the oven at 55 °C under vacuum for 24 h. The coating process was then repeated on the once-coated biosorbent to increase loading of chitosan on the alumina. Twenty-four hour were used in the second coating process. Excess oxalic acid in the composite biosorbent was neutralized by treatment with aqueous NaOH. The mixture was then filtered with Whatman 41 filter paper, washed with 2500 mL of DI water, and filtered. The twice-coated biosorbent was then dried in the oven under vacuum at 55 °C for about 48 h and transferred to a glass bottle for storage in desiccators.

Characterization of material

The prepared IDCA (iron doped chitosan coated activated alumina) were examined by Scanning Electron Microscopy (SEM) and X-Ray (EDX) analysis, Nitrogen adsorption isotherm, Fourier Transform Infrared Spectroscopy (FT-IR), Elemental analysis (C,H,N analysis) and Thermo gravimetric analysis (TGA).
Nitrogen adsorption isotherms for pore size distribution and surface area: The adsorbent (IDCA) prepared in this study were analyzed for the specific surface area, pore volume, and PSD by N_2-physisorption using Autosorb-1C instrument (Quantachrome, USA). In addition, chemisorption was also carried out to measure the active metal surface area. The multipoint Brunauer, Emmett, and Teller (BET) surface area was measured from the nitrogen adsorption/desorption isotherm. The BET isotherm equation is typically applied on the adsorption isotherm in P/P_0 range of 0.05 to 0.35. Prior to the measurement, the samples were degassed in an outgassing station to remove any adsorbed water or entrapped gases in the IDCA samples. The total pore volume was measured from the amount of vapor adsorbed at the relative pressure close to unity (0.9994).
Scanning electron microscopy and energy-dispersive X-ray (EDX) analysis: The field emission scanning electron microscopy (FE-SEM, Supra 40 VP, Zeiss, Germany) was used to observe the surface morphology of IDCA. The samples were gold coated to improve its conductivity to obtain good images. Additionally, EDX elemental spectra of a few spots on the samples were taken for determining the elemental compositions. We present here the representative images and spectra of the samples.
Fourier transforms infrared spectroscopy (FT-IR): The FT-IR spectra of unloaded Chitosan coated Activated Alumina (CCA), and loaded Iron Doped Chitosan Coated Activated Alumina (IDCA) with As(III) and As(V) were acquired by Tensor 27 (Bruker, Germany) in the attenuated total reflectance (ATR) mode using Ge crystal. The sample chamber was continuously purged with nitrogen during the measurement. A total of 100 scans were taken for each sample.

Elemental analysis (EA): The EA of carbon (C), hydrogen (H), nitrogen (N), and oxygen (O) of the various samples was carried out with the aid of the elemental analyzer (Model: CE-440 EL, Exeter Analytical Inc, US). The percentage C, H, N, and O contents were determined for the various samples.

X-ray diffraction analysis: It is difficult to directly examine the phase composition and pore structure of the alumina layers so the activated alumina powder was used as a substitute to be studied. Powder X-ray diffraction (XRD) analysis was undertaken to determine the structural parameters of the prepared iron doped chitosan coated activated alumina samples, using a Seifert X-ray generator (ISO Debyeflex 2002, Germany) for the Cu-kα radiation. The finely powdered sample was placed on a cleaned glass plate as a thin layer for analysis. The samples were analyzed from 10^o to 80^o (2θ) at the step size of 0.5°.

TGA and DSC analysis: Thermogravimetric analysis (TGA) of the organic inorganic biopolymer composite was recorded by a PerkinElmer Pyris Diamond thermogravimetric analyzer at a heating rate of 5°C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) of poly(butyl methacrylate) was carried out on a MDSC 2910 modulated differential scanning calorimeter (TA In- struments) at a heating rate of 5°C/min under a nitrogen atmosphere. TGA was measured with a Hi-Res TGA 2950 thermogravimetric analyzer (TA Instruments) attached to a thermal analyst 2100 (DuPont Instruments) thermal analyzer at a heating rate of 5°C/min under a nitrogen atmosphere.

Determination of arsenic

Total inorganic arsenic and As(III) analysis were carried out by spectrophotometric silver diethyl dithiocarbamate method (APHA, 1998). The lower limit of detection was found to be 4 µg. Each sample was analyzed twice. The co-efficient of variation in the duplicate samples was 2.5%. The average total arsenic level in 20 aqueous calibration check samples spiked with 50 µg As was 52 ±4.0 µg. Calibration was carried out daily with freshly prepared arsenic standards, before the sample analysis.

Results and discussion

Nitrogen adsorption isotherms for pore size distribution and surface area

The N_2 adsorption/desorption isotherms of the IDCA samples (**Fig. 1**) shows type-I sorption behavior with a hysteresis loop, pointing to the microporous structure characteristic [**36**]. The pore size distributions are classified in accordance with the classification adopted by the (IUPAC) of both the samples CCA and IDCA respectively, (**Fig. 2**, **Table 2**). A sharp initial rise in the low P/P_0 region can be observed in the IDCA, which indicate the presence of micropores in the material. It is evident from **Fig. 1** that the adsorbent possesses micropores. Though chitosan coating on activated alumina did not create significant increase in external surface area, however, it resulted in the formation of new pores. This observation manifests itself in the shift of pore size distribution maxima towards the lower pore size. **Table 2** shows the high surface area of iron doped chitosan coated activated alumina. The graph between pore diameter (Å) and Dv/(log d) ([cc/g]) (**Fig. 2**) clearly indicates the covered area of microporous characteristics.

SEM and EDAX

The surface morphology of IDCA characterized by SEM indicates a porous and fibrous structure (**Fig. 3**). The shapes of the adsorbent were spherical and the size of IDCA ranged from 0.8 mm to 0.9 mm. The surface was rough and folded due to the drying procedure. The geometry of porous alumina is as a honeycomb structure, which may be characterized by a close packed array of column hexagonal cells. The surface morphology of the iron doped chitosan coated activated alumina also exhibits grooves which indicate that the surface is etched due to incorporation of metals by impregnation [**37**]. The EDAX plot (**Fig. 4**) of IDCA shows the presence of carbon, oxygen, aluminum and iron.

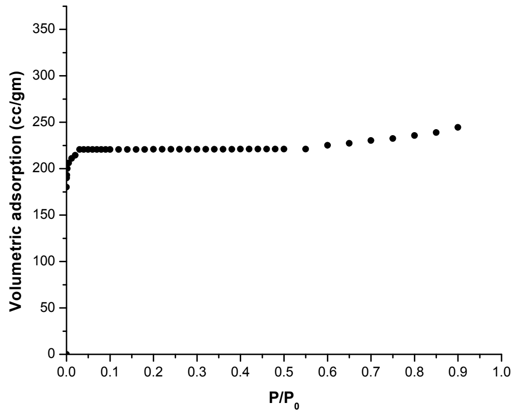

Fig.1. Nitrogen adsorption isotherm for IDCA.

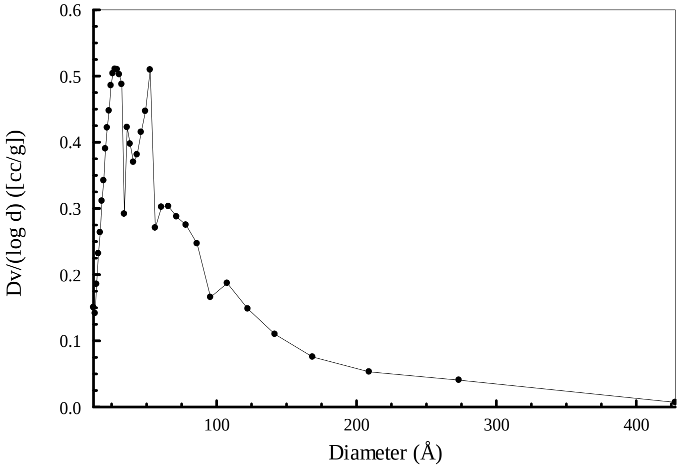

Fig. 2. The graph between pore diameter (Å) and Dv/(log d) ([cc/g]) for IDCA.

Table 1. Physical properties of based materials (activated alumina).

Sl. No.	Properties	DF-101	F-101
	PHYSICAL PROPERTIES		
1.	Physical State	Ball	Balls
2.	Particle Size	0.40 – 1.2 mm	0.40 – 1.2 mm
3.	Moisture % by mass	2.0 % Max	2.0 % Max
4.	Bed crushing strength	99% Max	99% Max
5.	Bulk Density gm/cc (Packed)	0.75 – 0.82	0.92 – 1.00
6.	Loss on Attrition %	0.5 % Max	0.5 % Max
7.	Pore Volume gm/cc	0.42 – 0.48	0.35 – 0.39
8.	Adsorption capacity at 30^{O}C & RH 60	20% min	18% min
9.	Surface Area, m^2/g	340 – 380	250 - 300

Table 2. Surface area and pore size distribution of CCA and IDCA.

Sl. No.	Surface area (m^2/gm)	Total pore volume (cc/gm)	PSD (%)		
			Meso (BJH)	Micro (MP)	Macro
1-CCA	299.0	0.2804	70.84	16.80	12.36
2-IDCA	370.9	0.3570	36.09	72.5	-

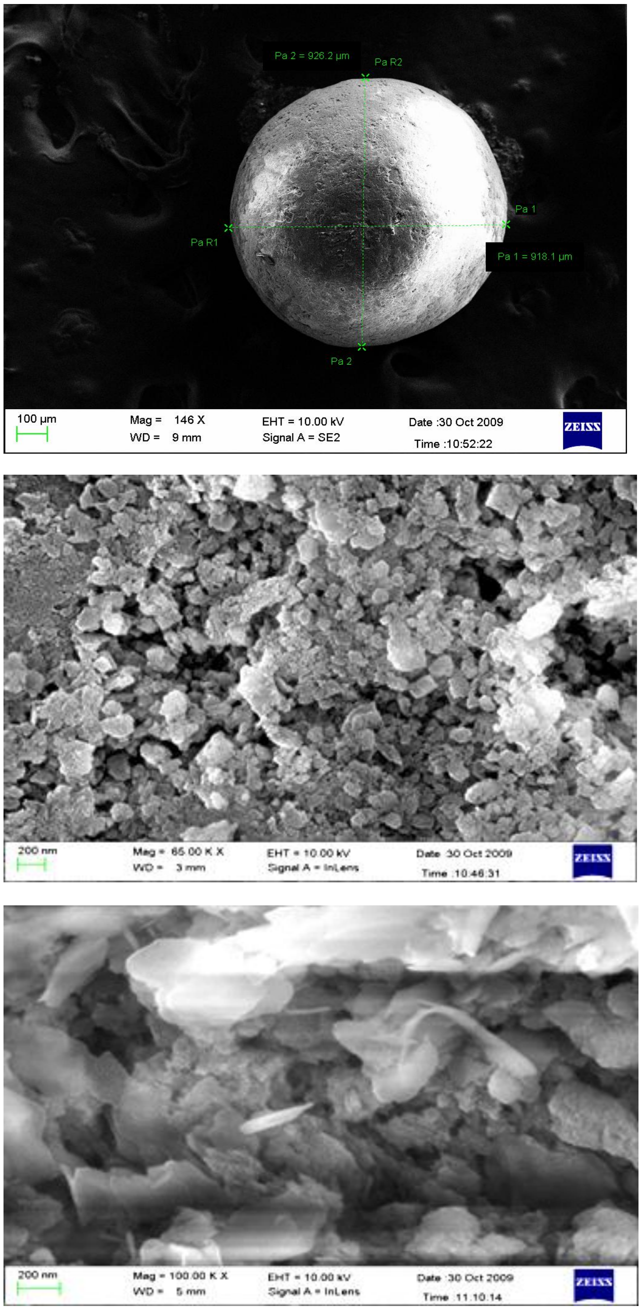

Fig. 3. SEM images of IDCA at various magnifications

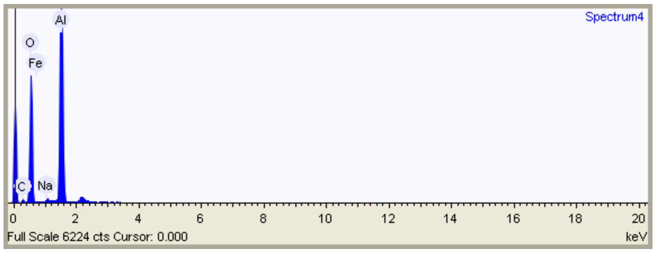

Fig 4. EDAX of the IDCA

Table 3. Elemental analysis of IDCA.

Element	Weight %	Weight % σ	Atomic %
Carbon	5.730	0.587	8.700
Oxygen	59.635	0.474	67.982
Sodium	0.789	0.094	0.626
Aluminum	33.313	0.335	22.518
Iron	0.533	0.084	0.174

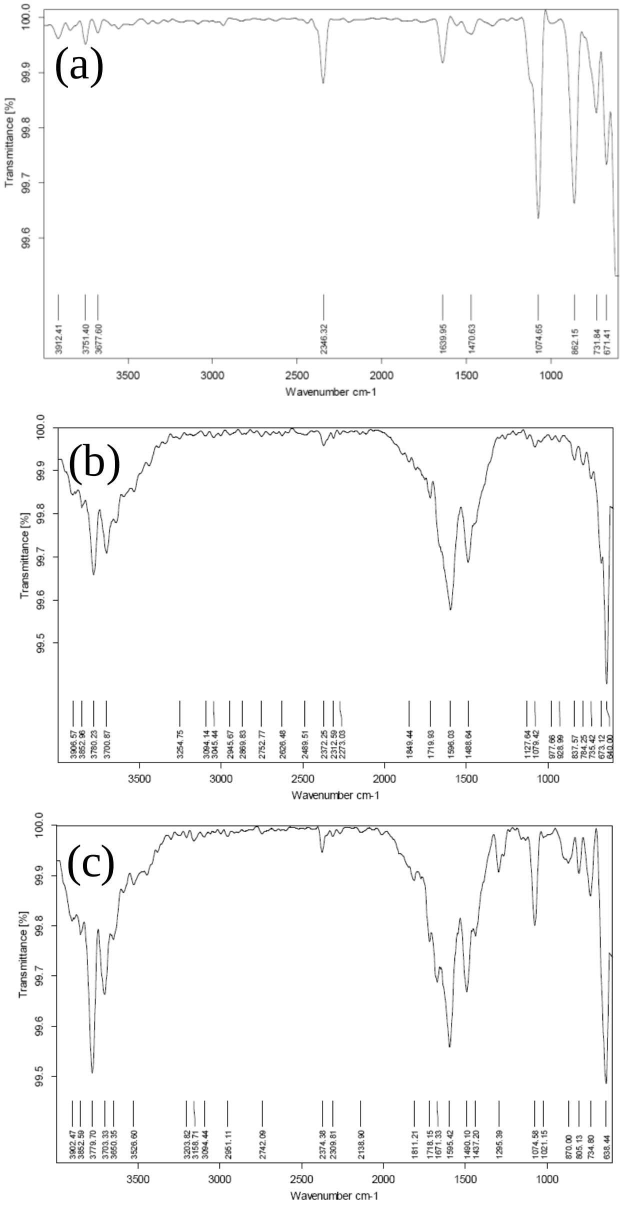

Fig. 5. FTIR spectra of (a) plain activated alumina, (b) chitosan coated activated alumina and (c) iron doped chitosan coated activated alumina (virgin).

Fourier-transform infrared (FTIR) spectra

The FTIR spectra of plain activated alumina, virgin chitosan coated activated alumina (CCA) and iron doped chitosan coated activated alumina (IDCA) are showing in **Fig 5a**, **5b**, and **5c** respectively. The FT-IR of alumina sample presented a band at 1639 cm^{-1} due to the δ(OH$_2$) of molecularity adsorbed water. Moreover, few weak intensity peaks rises at 3677 cm^{-1} and 3751 cm^{-1} showing non hydrogen bonded hydroxyl groups [**38**]. From the FTIR spectra of CCA and IDCA, it is evident that peaks at 3780, 3700 and 1596 cm^{-1} disappears due to electrostatic interaction of Fe with OH and NH$_2$ group of chitosan. A low intensity band at 1073 cm^{-1} is attributed to Fe-OH structural vibrations, suggests interaction of Fe with OH is not fully diminished.

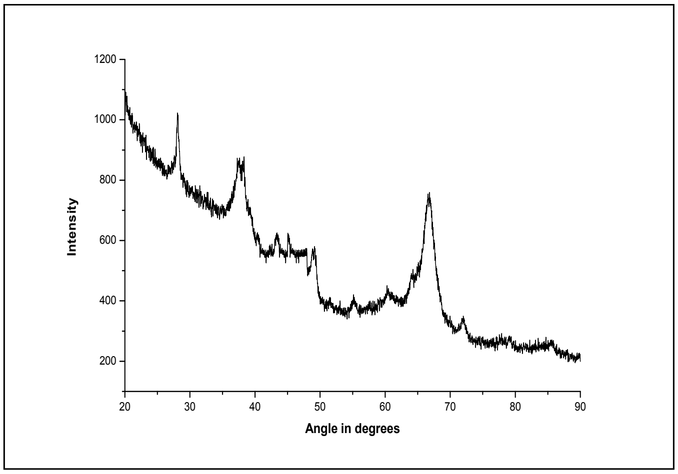

Fig. 6. XRD of iron doped chitosan coated alumina.

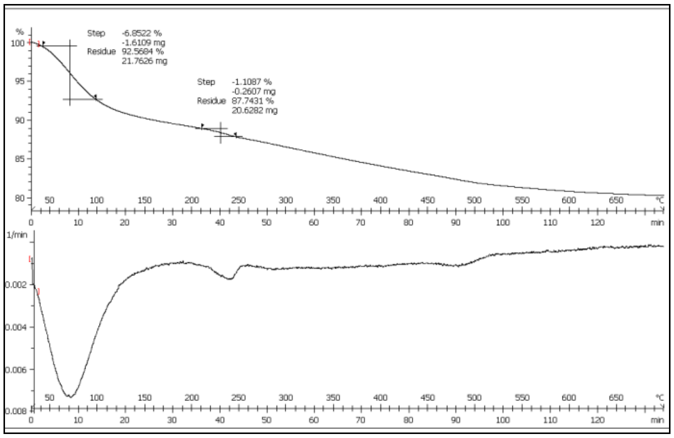

Fig. 7. TGA and DSC data curves displaying the mass loss of IDCA.

XRD analysis

In this study the X-ray diffraction patterns of (D/MAX-2400, Rigaku Co., Japan) of the iron doped chitosan coated activated alumina samples were studied. The main aim of XRD study is to observe the influence of iron on the surface of chitosan coated activated alumina. As shown in From (**Fig. 6**), there are four significant peaks observed at 2ɵ values of 28.2 (120), 38.4 (111), 45.7 (210), 65.1(220). The peak at 28.2 is assigned to aluminum oxide, 38.4, and 65.1are assigned to aluminum which is used as support. The strong peak at 45.7 is due to the presence of iron (iron chloride) which is doped to its enhanced adsorption capacity of arsenic. This result is in good agreement with EDX spectra discussed earlier.

DSC and TGA

DSC was an effective tool in characterizing chitosan and its metal complex. TGA curves and DSC scans of chitosan and chitosan–iron complex were taken. The scan of plain chitosan is not shown here. Chitosan degrades in two stages. The first stage starts at about 42 ^{o}C and second stage starts at 272 ^{o}C.

The chitosan–iron complex showed two degradation stages like the pure chitosan. The first stage of both started at about 44^{o}C with a weight loss (**Fig. 7**) due to the loss of water. However the second degradation stage of chitosan–iron complex took place at lower temperatures than that of the chitosan. This indicated that the chitosan–iron complex was formed during adsorption and was less stable than the chitosan itself.

An endothermic peak centered on 75^{o}C can be assigned to the evaporation of adsorbed water and water ligands. Chitosan did not show any endothermic transition between room temperature and 210^{o}C, indicating the lack of any crystalline or other phase change during the heating process.

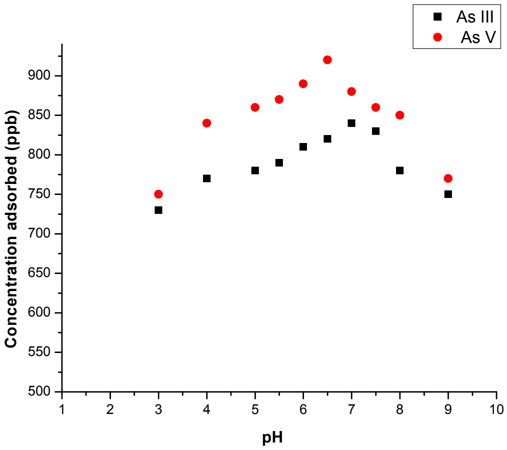

Fig. 8. Effect of pH on adsorption of As(III) and As(V) by IDCA.

Adsorption of arsenite and arsenate by IDCA

Adsorption was carried out using a batch method by adding 2.5 gm/L of Activated Alumina (AA), Plain Chitosan flakes (CF) and Iron doped Chitosan Activated Alumina (IDCA) to 20 mL of solutions containing various concentrations of arsenate and arsenite.

The effect of pH on the adsorption of As III and As V is summarized in **Fig 8**. It seems that the pH has little effect on the adsorptions of As III but maximum at neutral pH, whereas the adsorption of As V is favorable under near neutral pH 6.5. The efficient removal at neutral and near about pH 6.5 can be helpful in remediation of arsenic from real contaminated drinking groundwater.

From **Fig. 9**, it is evident that Plain chitosan was efficient in removing (0.06 ppm adsorbed out of 0.2 ppm initial concentration) 30 % of As(V) and 4% of As(III). In the case of Activated Alumina a significant removal rate of 50-85% was observed for As (V). A moderate percent removal capacity ranging from 40 – 55 % was observed for As (III). However, with IDCA as adsorbent there is remarkable high percent removal of > 90% (0.54 & 0.56 ppm out of 0.6 ppm initial concentration) for both the species of Arsenic (III) & Arsenic (V) respectively. This study demonstrated the potential use of IDCA in arsenic remediation filter units.

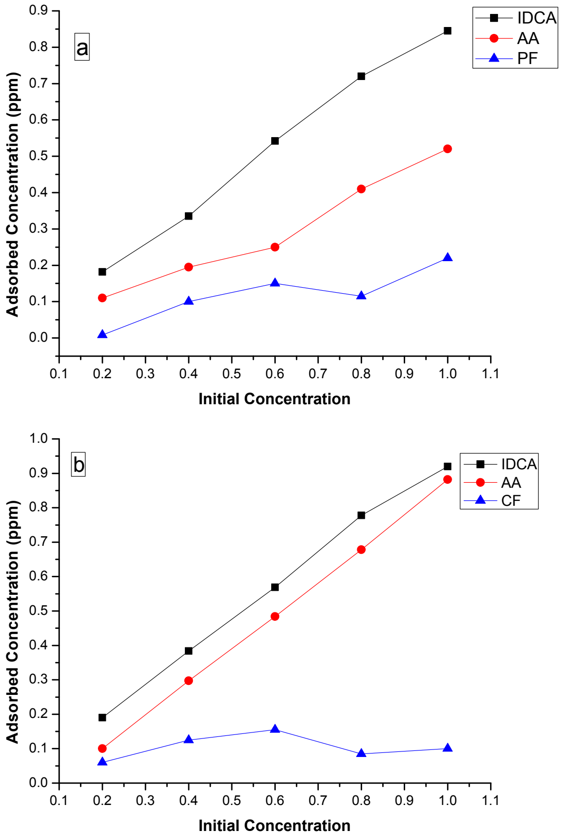

Fig. 9. Amount of (a) As(III) and (b) As(V) adsorbed for CF (Chitosan Flakes), AA (activated alumina) and IDCA (iron doped chitosan coated alumina) at different initial concentrations.

Mechanism of arsenic removal

Cavity provided by alumina gives more surface area for chitosan binding, as well as it also helps partially in the trapping of arsenic species when passed through it. It is evident that maximum adsorption of arsenic is observed for As(III) and As(V) at pH 6.5. The adsorption maximum at pH 6.5 is typical for As(V) but not for As(III). It has been reported that close to 100% As(V) adsorption was observed in the pH range of 4 – 8 by hydrated ferric oxide [**39**]. A similar observation is reported by many researchers for arsenate removal by either hydrated iron oxide or iron coated materials [**40-43**]. However, in the case of arsenite, it is possible that the reactive carbon groups present on the surface of the sorbent catalyze charge and redox transformation upon As(III) adsorption. FeOH$_4^-$ exists in high pH values and FeOH$_2^+$ in acidic solutions. Iron oxide surfaces are comprised of Fe(O,OH)$_6$ octahedra, in which arsenite or arsenate tetrahedra could be attached in different modes [**44**]. It is also well known that the pKa of chitosan ranges from 6.3-7.7 depending on the degree of deacetylation [**45**]. At neutral pH, it is reported that about 50% of the total amine groups in the chitosan remain protonated and theoretically available for the sorption of metal ions [**46**]. Hence, anionic arsenate ions are adsorbed on the chitosan backbone by simple ion exchange reaction. Elson et al. (1980) also reported that there exists chelation of arsenate and chitosan apart from electrostatic, ion exchange. It is also well know that alumina complexes with arsenate and arsenite wither by outer sphere or inner sphere depnding on pH [**47**]. Hence, from the above discussions it could be concluded that activated alumina, chitosan and iron play an important role in adsorption of arsenic from aqueous solutions.

Conclusion

A novel organic/inorganic polymeric composite was prepared using iron, chitosan and activated alumina. The prepared material has been characterized by various spectral techniques including, SEM, XRD, DSC, TGA, and FTIR. The applicability of the prepared adsorbent towards removal of both species of arsenic from aqueous systems has been demonstrated.

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