

## Adsorption potential of As (III) & As (V) from water using low cost modified natural sand

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**Abstract**—This article describes the potential of chitosan-coated sand (CCS) towards the removal of both As (V) and As (III). The study has investigated the feasibility of using modified natural sand for removing As (III) & As (V) from water as a function of pH, equilibration time, initial arsenic concentration, and adsorbent dosage. The adsorption data fitted well in the Langmuir model at different initial concentration of As (III) & As (V) at 2.5 g/l fixed adsorbent dose and follows pseudo first order reaction. Maximum adsorption of As (III) and As (V) for CCS is found to be 17 and 23 mg/l respectively, at pH 6.5 within 2 h of contact time.

biomaterial of high potential in various fields and its chemistry is quite significant. Chitosan, derived from deacetylation of chitin has been proved as an efficient adsorbent in the removal of arsenic from the drinking ground water [Gupta 2009]. Here in this paper, naturally occurring gangetic plain sand is modified by coating it with chitosan (CCS) in order to enhance its arsenic (As (III) and As (V)) removal efficiency from the water. This study evaluates the potential of CCS towards arsenic removal. Various experimental parameters including pH, reaction time, adsorption dose was systematically evaluated. Kinetic parameters and equilibration isotherms were also evaluated. The obtained data was successfully fitted to Langmuir model.

### I. INTRODUCTION

Arsenic contamination of drinking water has been a widely overlooked problem that has recently gained international attention. In recent years, arsenic (As) contamination of water and groundwater has become a major concern on a global scale [Mandal 2002 & Pendas 2000]. The enforcement of stringent standards for arsenic in drinking water by the regulatory agencies such as WHO calls for pragmatic approach in developing a suitable and cost effective technology to remove arsenic from drinking water.

Conventional water treatment processes involves the removal of toxic metal ions through sorption. Advanced water treatment techniques, which can be used as either primary treatment or post treatment, involve ion exchange, reverse osmosis, adsorption, coagulation, precipitation, adsorption-coprecipitation with hydrolyzing metals, and so on [Nikolaidis 2003]. Among these, adsorption currently appears to have the best potential for overall treatment, and it can be expected to be useful for a wide range of compounds. Chitin is the second most abundant biopolymer next to cellulose. It has become one of great interest not only as under-utilized resources but also a new functional

### II. EXPERIMENTAL

All reagents are of AR grade. A stock solution of As (III) and As (V) was made using milli - Q water. Standard acid and base solutions (10% H<sub>2</sub>SO<sub>4</sub> and 10%NaOH) were used for pH adjustments. Sodium arsenate hydrate, Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O and sodium arsenite NaAsO<sub>2</sub> (Merck reagent) are used to prepare stock solution of As (III) &As (V) standards. All standard solutions were prepared fresh daily and suitable dilutions is carried out.

Chitosan coated sand was prepared by using gangetic belt sand near Kanpur district. Initially the sand was sieved to a geometric mean size of 0.3 mm rinsed with deionized distilled water twice and dried at 90 °C for 20 hr. Chitosan was dissolved in 0.05 M acid to make the final concentration of 0.5% by weight. Finally, chitosan solution was stirred overnight and filtered to remove any suspensions. Now, the above heated sand was mixed with the dissolved chitosan solution and stirred for overnight. Effective coating of chitosan on the sand was achieved in two steps. The coated sand was washed with deionized distilled water and dried at room temperature for the further experiments.

To study the effect of initial pH (2–10) on arsenic uptake, experiments were performed with initial arsenic concentrations of 1000  $\mu\text{g/l}$  at a fixed contact time of 2 h. The effect of contact time was studied with an initial arsenic concentration of 1000  $\mu\text{g/l}$  and adsorbent dose of 2.5 g/l; pH was kept at 6.5 and contact time was varied from 15 to 240 min. Isotherm studies were conducted with varying initial As (III) and As (V) concentrations (100–1000  $\mu\text{g/l}$ ), fixed adsorbent dose of 2.5 g/l, and contact time of 2 h at pH 6.5.

All the analysis containing arsenic was carried out in Inductive Coupled Plasma Mass Spectroscopy (ICP-MS) (Thermo).

### III. RESULTS AND DISCUSSION

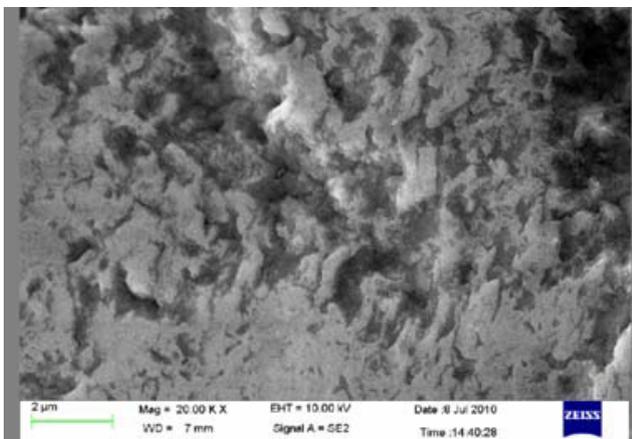


Fig1(a) Chitosan Coate Sand

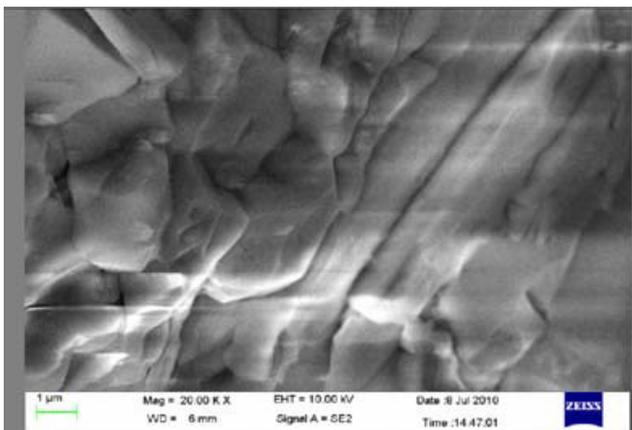


Fig1(b) Chitosan Coated Sand Loaded with As (III)

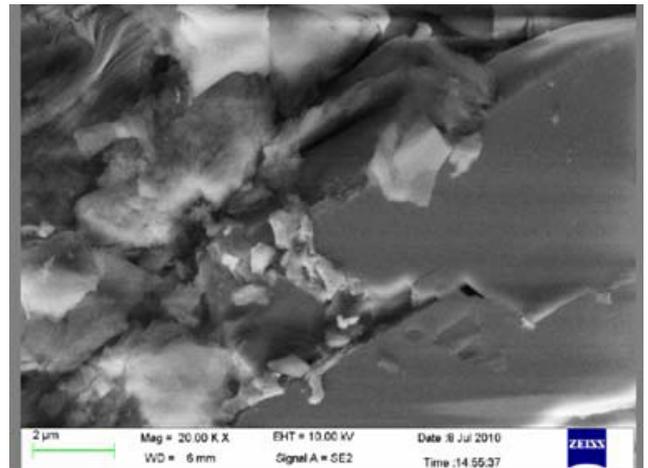


Fig 1 (c) Chitosan coated Sand Loaded with As(V)

The field emission scanning electron microscopy (FE-SEM, Supra 40 VP, Zeiss, Germany) was used to observe the surface morphology of CCS before and after loading with arsenic. The samples were gold coated to improve its conductivity to obtain good images. We present here the representative images of the samples (Fig. 1). The above SEM images indicates that change in surface morphology after the loading of As (III) and As (V) .

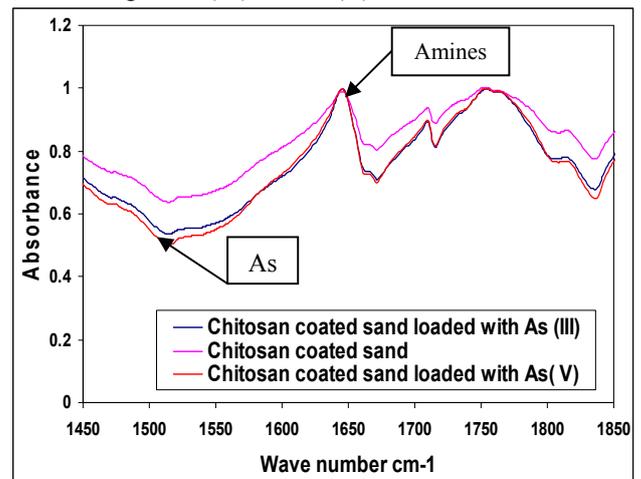


Fig 2. FTIR Spectra of Virgin and Loaded CCS

The FTIR spectra of unloaded CCS and loaded CCS with As (III) and As (V) were acquired by Tensor 27 (Bruker, Germany) in the attenuated total reflectance (ATR) mode using Ge crystal (Fig.2). The sample chamber was continuously purged with nitrogen during the measurement. A total of 100 scans were taken for each sample.

The above FT-IR spectrum clearly shows the presence of chitosan with amino and hydroxyl groups in the adsorbent material. Peak at  $1650\text{ cm}^{-1}$  corresponds to the amine group present in all the three spectra's where as  $1500\text{ cm}^{-1}$  shows the presence of As (III) and As (V) in the material after adsorption.

### Effect of pH

The solution pH is an important factor for all water treatment processes because it affects the speciation of metal in water. It is evident from Fig.3 that with increase pH from 1 – 6.5 there exists an increase in the adsorption capacity. With subsequent increase in pH resulted in decreased capacity. The same observation was prevalent in both As (III) and As (V) species. This observation could be attributed to the different forms of arsenic species at different pH values.

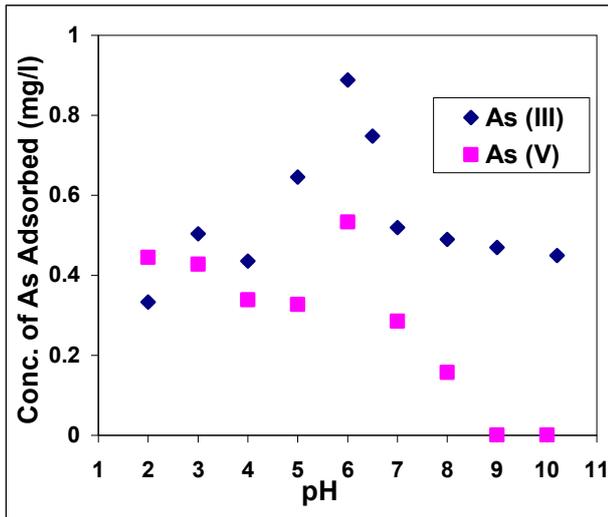


Fig.3 Optimization of pH

### Effect of Contact Time

Fig. 4 shows that As (III) and As (V) adsorption increased with an increase in contact time and the pseudo-equilibrium was achieved after approximately 2 h. Such a short adsorption time was probably due to the efficient reaction caused by the adsorbent composition of the materials.

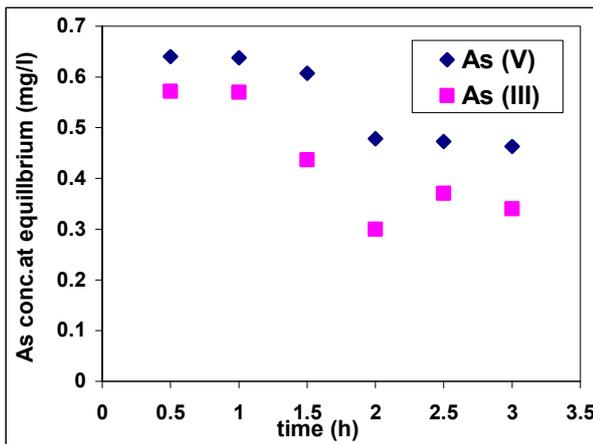


Fig. 4 Variation of Equilibration time

The experimental data were analyzed using a pseudo-first-order equation (1)

$$K = \frac{2.303}{t} \log \frac{C_0}{C} \quad (1)$$

where,  $C_0$  and  $C_e$  are the amount of initial As taken and amount of Arsenic adsorbed at pseudo equilibrium condition and at time  $t$ , respectively, and  $K$  is the adsorption rate constant. The Rate constant for As(V) and As(III) was found to be 1.0948 and 0.38078 respectively.

### Adsorption isotherms

Equilibrium adsorption isotherm studies were conducted with aqueous solutions of As (III) and As (V) varying the concentration from 100 to 1000  $\mu\text{g l}^{-1}$ . The adsorption isotherms are fundamental in describing the interactive behavior between solute and adsorbent (Ofomaja 2006). The isotherm yields certain constant values, which express the surface properties and affinity of the adsorbent. It also plays an important role in the design of an adsorption system. The Langmuir models are often used to describe equilibrium adsorption isotherms. The most widely used Langmuir equation (2), is valid for monolayer sorption on to a surface with a finite number of identical sites. It is assumed that once a metal ion occupies a site, no further adsorption can take place at that site (Ho et al., 2002).

$$C_e/q_e = C_e/Q + 1/Qb \quad (2)$$

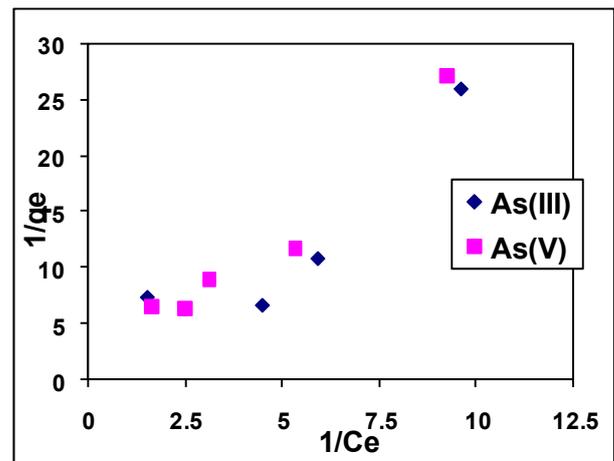


Fig.5 Graphical representation of Langmuir isotherm for As (III) & As (V)

TABLE 1: LANGMUIR ISOTHERMS CONSTANT

Langmuir model parameters			
Species	R <sup>2</sup>	Q <sub>max</sub> (mg/g)	b(ml/mg)
As III	0.8172	17	1.144
AS V	0.9465	23	1.016

The calculated results of the Langmuir isotherm constants are given in Table 1 with Langmuir monolayer adsorption capacity to be 17 mg/g and 23 mg/g at pH 7 for As (III) and As (V) respectively.

TABLE 2: COMPARISON OF MAXIMUM ADSORPTION CAPACITY (mg/g) OF SOME ADSORBENTS (pH IS SHOWN IN PARENTHESIS)

Adsorbents	Capacity (mg/g)		Reference
	As (III)	As (V)	
Goethite	10.1 (7.5)	12.1 (7.5)	Javier et al. 2007
Hematite	10.0 (7.3)	31.3 (7.3)	Javier et al. 2007
Bone Char	4 (7)	4.58 (7)	Mlilo 2010
Iron oxide coated sand	0.136 (7.6)	-	Thirunavukkarasu et al 2005
FeS-coated sand	10.7 (7)	-	Young-soo-han et al 2010
Iron Coated Chitosan	16 (7)	22.5 (7)	Gupta et al 2009
Iron doped phenolic resin	13(6.5)	5 (6.5)	Sharma et al 2010
Chitosan Coated Sand	17(7)	23 (7)	Present study

The table above (Table 2) shows the comparison of adsorption capacity of the different adsorbent used for the removal of arsenic (As (III) and As (V)) from the arsenic contaminated water at different pH .

#### IV. CONCLUSIONS

Chitosan coated sand have a high maximum adsorption capacity and adsorption was found to be maximum within 2h. Further, the adsorbent was found to be efficient in near neutral pH conditions. The ability of chitosan coated sand to adsorb both As (III) and As (V) simplifies the treatment process of the ground water purification. The adsorption capacity obtained was found to considerably higher than the plain or iron coated sand. It should also be mentioned that the material used in this study is inexpensive. Hence, to tackle arsenic contamination, chitosan coated gangetic plain sand could be an attractive adsorbent material. Future research could focus on regeneration of material, to study the effects of interfering anions and its applicability to the decontamination of Arsenic in real groundwater.

#### ACKNOWLEDGMENT

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#### REFERENCES

- [1] Elson, C.M., Bem, E.M. and Ackman, R.G., "Removal of arsenic from contaminated drinking water by a chitosan/chitin mixture", *Water Research*. 1980, 14 (9), pp 1307-1311.
- [2] Gupta, A., Chauhan V., and Sankararamkrishnan, N., "Preparation and Evaluation of iron - chitosan composites for removal of As(III) and As(V) from arsenic contaminated real life groundwater", *Water Research*. 2009, 43 (15) pp. 3862-3870.
- [3] Javier, G., Maria, M., Joan de, P., Miquel, R. and Lara, D. Arsenic sorption onto natural hematite, magnetite and goethite, *Journal of Hazard Material*. 141 2007, pp. 575–580.
- [4] Kabata-Pendias, A. and Pendias, H., "Trace elements in soils and plants", CRC Press, Boca Raton, FL, 2000.
- [5] Han, Y.-S., Gallegos, T.J., Demond, A.H., Hayes, K.F. "FeS-coated sand for removal of arsenic(III) under anaerobic conditions in permeable reactive barriers", *Water Research*, 2010 Article in Press 1-12.
- [6] Ho, Y.S., Huang, C.T, and H.W. Huang, "Equilibrium Sorption Isotherm for Metal Ions on Tree Fern," *Process Biochem.*, 2002 , 37 pp.1421–1430.
- [7] Mandal, B.K., Suzuki, K.T., "Arsenic round the world: a review", *Talanta* . 2002,58 pp. 201–235.
- [8] Mlilo, T.B., Brunson, L.R., Sabatini, D.A. "Arsenic and fluoride removal using simple materials" *Journal of Environmental Engineering*. 2010,136 (4), pp. 391-398.
- [9] Nikolaidis, N.P., Dobbs, G.M. and Lackovic, J.A., "Arsenic removal by zero-valent iron: field, laboratory and modeling studies", *Water Research*. 2003, 37 p.1417.
- [10] Ofomoja, A.E. and Y.S. Ho, "Equilibrium Sorption of Anionic Dye from Aqueous by Palm Kernel Fibre as Sorbent," *Dyes and Pigments*. 2006, 12 pp. 249- 257.
- [11] Sharma,A., Verma,N., Sharma, A., Deva, D. and Sankararamkrishnan,N."Iron doped phenolic resin based activated carbon micro and nanoparticles by milling: Synthesis, characterization and application in arsenic removal", *Chemical Engineering Science*. 2010, 65 pp. 3591–3601.
- [12] Smedley, P.L. and Kinniburgh, D. G "A review of the source, behavior and distribution of arsenic in natural waters", *Applied Geochemistry*. 2002, 17 pp.517–568.
- [13] Thirunavukkarasu, O.S., Viraraghavan, T., Subramanian, K.S., Chaalal, O. and Islam, M.R., "Arsenic removal in drinking water - Impacts and novel removal technologies" , *Energy Sources*. 2005, 27 (1-2) pp 209-219.