An insight into As(III) adsorption behavior on β -cyclodextrin functionalized hydrous ferric oxide: Synthesis & characterization

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ABSTRACT: The particular study explores the adsorption potential of As(III) on β -cyclodextrin functionalized hydrous ferric oxide (HCC). This is characterized by XRD, FESEM, AFM, XPS, BET, surface site concentration and FTIR. The modification of hydrous ferric oxide (HFO) surface by β -cyclodextrin provides copious –OH groups which in turn enhances As(III) adsorption on HCC compared to HFO. The adsorption remains almost constant in pH range 3–8 which decreases at higher pH (>8) and followed monolayer and pseudo first order kinetics. It is spontaneous at 303 K with increasing entropy and decreasing enthalpy. Thus HCC is found to be a more efficient adsorbent media compared to HFO.

1 INTRODUCTION

The metalloid arsenic (As) which has been inflicting havoc on mankind for the past few decades and has assumed global proportions transcending geographical boundaries and communities, has targeted water which is the support system of a civilization as the medium for its transportation into the environment and biological systems which explains the countless deaths it has left behind in its wake (Biswas *et al.*, 1998; Smedley & Kinniburgh, 2002). The cases of As poisoning through drinking water can be traced long back in the world history (Ritchie, 1961; Vaughan, 2006; Wang *et al.*, 2007). In 1898, the first cases of skin cancer were observed among population consuming As contaminated water in Poland. Since then it has been conclusively established that unabated ingestion of As via drinking water causes a variety of carcinogenic effects of skin, liver, kidney and other organs which ultimately leads to death. All these incidents have led to World Health Organization (WHO) and other national agencies to fix the permissible limit to $10 \mu\text{g L}^{-1}$ of As in drinking water. The principle source of As contamination is groundwater and the majority of rural and semi urban population in vast parts of the globe depend on this form of water for their drinking water and other household needs. The problem associated with As contamination is severe in Bangladesh and major parts of West Bengal, India. In West Bengal, more than 6 million people from 12 districts covering 111 blocks are worst affected and consuming drinking water with As concentration $>50 \text{ mg L}^{-1}$ (Mazumder *et al.*, 2010). The present investigations provide promising results demonstrating that HFO modified by β -cyclodextrin

would be a better scavenger of As(III) from contaminated groundwater as against conventional pure HFO.

2 METHODS/EXPERIMENTAL

A ferric chloride solution was prepared in 0.1 M HCl and mixed with an aqueous solution of β -cyclodextrin. The mixture was warmed at 90°C accompanied by gradual addition of dilute NH_3 solution with constant stirring till the pH reached around 7. The dark brown precipitate formed was aged for 48 h, filtered, and washed repeatedly with deionized water. The filtered mass obtained was dried at 100°C into an air oven. The fully dried mass was ground in a mortar and sieved to obtain a particle size between 52–100 mesh (250–150 microns) and subsequently used for adsorption studies.

3 RESULTS AND DISCUSSION

Figure 1A shows the XPS spectra of HCC. The peak at 711.9 eV (spectrum 1B) is due to the 2p electron of Fe and peak at 532.0 eV (spectrum 1C) value indicates the O 1s electron. The peak at 286.1 eV showed the presence of C-OH/C-O-C bonds on the HCC surface which clearly reveals that HFO was modified with β -cyclodextrin.

As(III) adsorption was observed to slightly decrease up to pH_i 8.0 for HCC. Above this pH_i value the adsorption decreased markedly up to pH 11.0. At pH_i 7.0, 65.8% As(III) uptake was observed for pure HFO whereas for HCC 81.5% of the total As(III)

were removed from solution. When the initial solution pH was raised to 9.0 the As(III) adsorption dropped down to 66.3% for HCC. The pH_{ZPC} value of HCC lied within the range 7.6–7.9 indicating that below this pH range the surface charge of HCC was positive and above it surface becomes negative. At low pH the most dominant form of As(III) species present in the solution is $\text{As}(\text{OH})_3$ ($\text{pK}_1 = 9.2$). Due to the presence of large number of surface $-\text{OH}$ groups the neutral $\text{As}(\text{OH})_3$ species form strong H-bond with HCC surface at low pH region.

4 CONCLUSIONS

Hydrous ferric oxide (HFO) has proven to be a potent adsorbent for dissolved As(III) in contaminated water. However, surface modification of HFO with β -cyclodextrin by a simple and economical route shows large enhancement of As(III) scavenging power. The systematic As(III) adsorption by this material has showed that the optimum pH and equilibrium contact time are $\sim 7.0 \pm 0.1$ and 120 min, respectively. The pseudo first-order equation describes the kinetic data (pH, 7.0 ± 0.1 ; temperature, 303 ± 1.6 K) well. The equilibrium data (pH, 7.0 ± 0.2 ; temperatures (± 1.6 K), 288, 303, 318 and 333) fit very well with the Langmuir isotherm model. The Langmuir monolayer adsorption capacity is 66.96 ± 9.16 (mg of As per g. of HCC) at 303 K, and that increases

Figure 1. XPS of (1A) HCC, (1B) Fe 2p spectrum and (1C) O 1s spectrum.

with increasing temperature. The adsorption reaction is spontaneous ($\Delta G^\circ = \text{negative}$) and exothermic ($\Delta H^\circ = \text{negative}$), and that takes place with increasing entropy ($\Delta S^\circ = 0.007$). The energy (kJ mol^{-1}) of As(III) adsorption and the FTIR analysis have suggested that the As(III) adsorption on HCC is of both physisorption as well as chemisorption in nature. The As(III) adsorption by HCC is negatively influenced by phosphate and sulfate ions. The regeneration of As(III) adsorbed material is possible maximum up to 75% with 1 M NaOH solution.

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