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Surface-modified zeolite–A for sequestration of arsenic and chromium anions

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It is of immense practical importance to develop materials with tailored properties to sequester anionic pollutants in addition to cationic pollutants. Zeolites are alumino-silicate materials with properties to attract positive-charged ions and, therefore, are widely used for sequestration of cationic pollutants. Surface-modified zeolite materials have been developed from commercial zeolites and flyash-based zeolites by treating them with surface modifiers like hexadecyltrimethylammonium bromide and tetramethylammonium bromide. The adsorbent has been evaluated for removal of arsenic and chromate anions. High selectivity, faster kinetics and high adsorption capacity ensure-cost effectiveness of these materials compared to other conventional materials for de-arsenification.

Keywords: Arsenic, chromium, flyash-based zeolite, surfactant-modified zeolite, water treatment.

IN the backdrop of the widespread public concern about vast sections of population in West Bengal (India) and Bang-

ladesh being exposed to groundwater containing high concentration of arsenic, the urgency for delineating appropriate treatment strategy for arsenic removal is realized to overcome the grave threat of chronic arsenic poisoning. Recent epidemiogical evidence of the toxicity of inorganic arsenic suggests that the current maximum contaminant level (MCL) may not be sufficiently protective for human health; the probable WHO guideline value of 10 μg/l is based on both estimated health risks and the practical quantitation level. The estimated cost of compliance with more stringent levels (in the range 2–20 μg/l) is quite high. The existing treatment technologies, such as coagulation, softening, and adsorption on alumina or activated carbon and reverse osmosis accomplish arsenic removal to meet the current standard of 50 μg/l. However, imposition of low arsenic MCL is likely to require implementation of new treatment practices or significant modification of the existing treatment practices. It needs to be emphasized that only a few de-arsenification technologies in vogue have been successfully demonstrated in the field. To achieve this stringent target, novel materials need to be developed wherein zeolites are emerging as potential materials, which can be suitably functionalized to target specific pollutants of concern. Zeolites are hydrated crystalline aluminosilicates with uniform pore size, reversible hydration and ion exchanging, sorptive and sieving ability. These characteristics can be exploited for targetting anionic species. It is challenging to tackle anionic pollutants using faujasitic zeolites and it has been achieved by modifying the surface of zeolites to selectively target anions.

Li and Bowman[1] have studied the removal of oxyanions, viz. nitrate, arsenate, chromate, etc. using surface modified clay. Natural kaolinite was treated with hexadecyltrimethylammonium bromide (HDTMA–Br) to a level twice that of the cation exchange capacity. Sorption of each oxyanion was well described by the Langmuir isotherm. Desorption of bromide counter ion indicated that each of the oxyanions was retained by ion exchange on HDTMA–Br bilayer formed on the organo-kaolinite. It was unaffected by solution in the pH range of 5–9, but at pH 11 the bilayer was affected due to competition of OH⁻ for the anion exchange sites. The results demonstrated that properly prepared organoclays could remove oxyanions as well as non-polar organics from contaminated water.

The adsorption of chromate by surface-modified clays like kaolinite and montomorillinonite modified with cationic surfactant HDTMA–Br bromide was reported[2]. It was observed that the amount of chromate absorbed is dependent on pH; the removal goes on decreasing with increasing pH; becomes negligible over pH 8. Clays also have the inherent disadvantage of swelling and shrinkage associated with them and therefore cannot be used effectively for treatment purposes.

Li et al.[3] have reported that planar nitrate sorbs more on surfactant-modified zeolite surface than tetrahedral chromate. In the presence of sulphate or nitrate, chromate sorption is hindered due to competition for sorption sites. Quantitative sorption of nitrate and chromate and desorption of bromide indicate that the sorption of oxyanions is primarily due to surface anion exchange. However, the material has limited exchange potential due to limited exchange capacity of natural zeolite.

Bowman et al.[4] had studied the uptake of the surfactants HDTMA–Br by a natural clinoptilolite-rich zeolite and subsequent retention of aqueous solutes. Surface-modified zeolite (SMZ) showed weak sorption capacity for cations such as Pb (II), Sr (II), and strong sorption for anions such as CrO_4^{2-}. This is in contrast to natural zeolite, which is a good cation exchanger. The results suggested formation of stable HDTMA–Br bilayer on the external surface of zeolite, which retained anions via anion exchange mechanism. SMZ thus proved to be a useful sorbent for anion removal. However, natural zeolite by virtue of its low exchange capacity and other associated impurities, sorbs anion to a lower degree, which can be improved using synthetic zeolites.

Vujakovic et al.[5] had tested the adsorption of sulphate, hydrochromate and dihydrogen phosphate anions on surfactant-modified clinoptilolite. SMZ was prepared by the adsorption of cis-1 aminooctaden-9 (oleyamine) on both modified and unmodified natural clinoptilolite. It was observed that oleyamine adsorbed on H^+-clinoptiolite by protonation of NH_2 group showed strong anion-adsorbing tendency compared to Ca- and Na-clinoptilolite derivatives, which are weak anion adsorbents. The differences in anion adsorption are attributed to the fact that oleylamine forms hydrogen bonds with Ca and Na-clinoptilolite and thus yields insufficient adsorption sites for anions.

Klatte and Cadena[6] developed a process for coating zeolite crystals with paraffin. Zeolite crystal having pores coated with wax, fat, oil, or a mixture of at least one quaternary ammonium cation (QAC) and wax, fat, or oil, are positively charged and have a tendency to attract anions. The coating of paraffin/wax applied to zeolite crystals prior to adsorption of QAC may limit their application for removal of anions; specifically arsenic from drinking water.

This communication addresses the synthesis of SMZ and its evaluation for removal of oxyanions.

All chemicals used were of purest research grade available. The materials used are NaA zeolite (Degussa, Germany) and HDTMA–Br (all E-Merck grade).

The flyash used for this synthesis was collected from Koradi Thermal Power Station (KTPS), Koradi, Nagpur, India. Sieved and iron-removed flyash was used for the synthesis of flyash based zeolite A (FAZ-A). Flyash and sodium hydroxide pellets in the ratio 1 : 1.2 were crushed in a grinder and the crushed mass was subjected to fusion at 600°C for 90 min. After cooling of the fused mass, it was again subjected to crushing for homogenization and its slurry was prepared by adding double distilled water. To the slurry was added a measured volume of sodium aluminate solution and this mixture was subjected to

Table 1. IR frequencies for different zeolite samples and standard zeolite-A

	Frequency reported in the literature					
Sample	Peak-1 995 cm^{-1}	Peak-2 464 cm^{-1}	Peak-3 660 cm^{-1}	Peak-4 550 cm^{-1}	Peak-5 3400 cm^{-1}	Peak-6 1645 cm^{-1}
Degussa	1004.8	464.8	667.3	559.3	3402.2	1651
FAZ-A	999.1	472.5	667.3	567.0	3413.8	1651
SMZ-A	1004.8	466.7	667.3	555.5	3421.5	1654.8

overnight stirring. Subsequently, this slurry was transferred into a Teflon vessel and kept in an oven at 100°C for 3 h for hydrothermal crystallization. The crystallized mass was cooled, filtered and washed thoroughly. The filtered cake was then oven-dried for 6–8 h and homogenized for further use. The synthesis method is described in detail elsewhere[7].

Zeolite was washed with distilled water several times till its pH reaches to 10.0 to 10.5. Pre-weighed quantity of washed zeolite sample was then mixed with different initial concentrations of surfactant, i.e. HDTMA–Br solution in 1 : 100 (solid : liquid) ratio. The surfactant concentration ranged from 500 to 5000 mg/l for 10 g of zeolite. The solution was agitated for 7 to 8 h at 150 rpm on a shaker at pH 8.0 to 8.5. The solution was then filtered and the solid residue was washed with double-distilled water and air-dried for 4 to 6 h. The residual solution was analysed by TOC and the loading achieved for HDTMA–Br was in the range 10–90 mg/g. HDTMA–Br forms a bilayer for concentration greater than 328 mg/l.

The SMZ-A sample synthesized as such was then mechanically ground with a mortar and pestle to fine particle size. SMZ having variable surfactant loading was then used for removal of arsenic. The same procedure was repeated for modification of commercial zeolite-A samples as above for comparative studies. The different SMZ samples having different surfactant loading were then used for removal of arsenic in water.

Pre-weighed quantity of SMZ was mixed with 25 ml solution of As or Cr with initial concentration ranging from 2 to 25 mg/l. The pH was maintained in the range 6.5 to 7 by addition of dilute HCl. The mixture was then kept for shaking at 150 rpm and the solution was filtered. The filtrate was analysed for As and Cr using AAS and ICP.

Zeolite is found to exhibit a typical infrared spectroscopic pattern. The spectra can be grouped in two classes. The first is due to internal vibration of the TO_4 tetrahedron which is the primary unit of structure and is not sensitive to other structural vibration. It is found in the range 950–1250 cm^{-1} and 420–500 cm^{-1}. Strongest vibration at 950–1250 cm^{-1} is assigned to the T–O stretching, and the next strongest band at 420–500 cm^{-1} is assigned to the T–O bending mode. The stretching modes are sensitive to the Si–Al composition of the framework and may shift to a lower frequency, while the bending mode may be related to

the linkages between tetrahedral. The second type of vibration is sensitive to the overall structure and the joining of the individual tetrahedra in secondary structural unit as well as their existence in the large pore openings. The IR peaks observed for FAZ-A (Figure 1 a) are presented in Table 1 and match closely with that reported in the literature[3].

The IR spectra of SMZ-A is presented in Figure 1 b. The major peaks for SMZ-A are observed at 1004.8, 466.7, 667.3, 555.5, 3421.5 and 1654.8 cm^{-1}, which are comparable with the peaks of FAZ-A except for additional peak observed near 2800 cm^{-1}. This intense peak at 2800 cm is also observed in pure HDTMA–Br.

The IR peaks observed for zeolite-A (Degussa), FAZ-A and SMZ-A are similar, indicating structural stability of the sample.

XRD analysis was used to determine the structural properties of SMZ-A. The XRD of SMZ-A is represented in Figure 2. On comparing the XRD data of SMZ with those of FAZ-A, it was observed they closely resembled with each other with slight differences in 2θ and d-spacing values, indicating that the structural integrity of the sample is retained on surfactant treatment.

SMZ-A has been evaluated for arsenic and chromate removal. Effects of various parameters such as surfactant loading, initial anion concentration, pH and dose of zeolite on anion removal efficiency were considered. Each of these parameters has been discussed below.

Figure 3 shows the effect of loading of surface modifiers (HDTMA–Br and tetramethylammonium bromide (TBA–Br) on As removal. The per cent As removal increases initially with HDTMA–Br loading and shows a maximum value of 82.34 at a surfactant loading of 800 mg/l. Further increase in surfactant concentration results in decrease in per cent As removal. Thus treatment with initial concentration of 800 mg/l of surfactant appears to be the optimal loading for As removal. This initial concentration exceeds the critical micelle concentration of the surfactant. It is therefore envisaged that these micelles attach as such to the external surface and then rearrange to form a bilayer that tends to impart anionic characteristics[4]. The trend observed for TBA–Br loading is different compared to HDTMA–Br. It shows maxima at 200 mg/l surfactant loading with further fall up to 1000 mg/l and then again increases to around 40% removal. Considering the carbon chain length, HDTMA–Br is more hydrophobic compared to
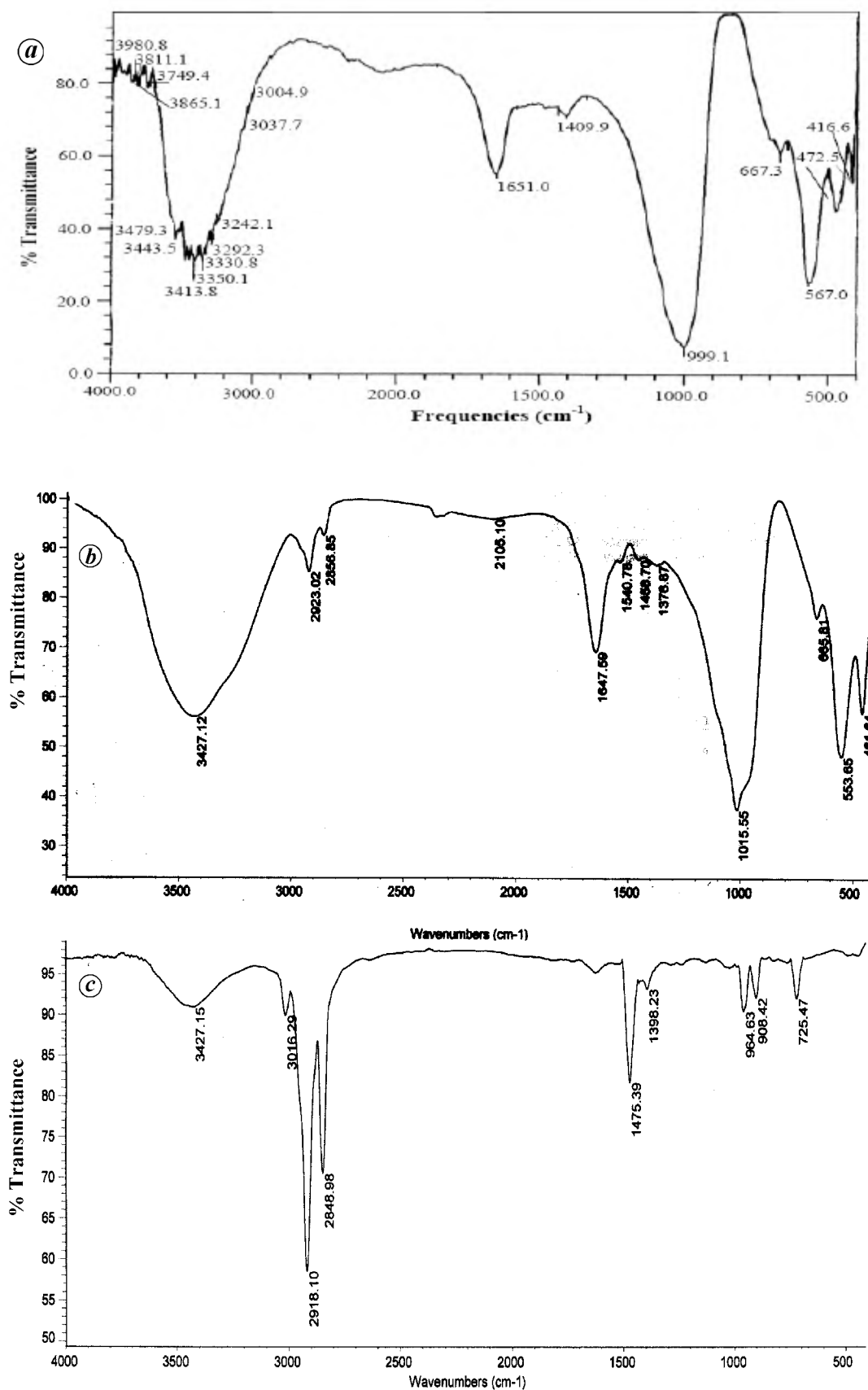
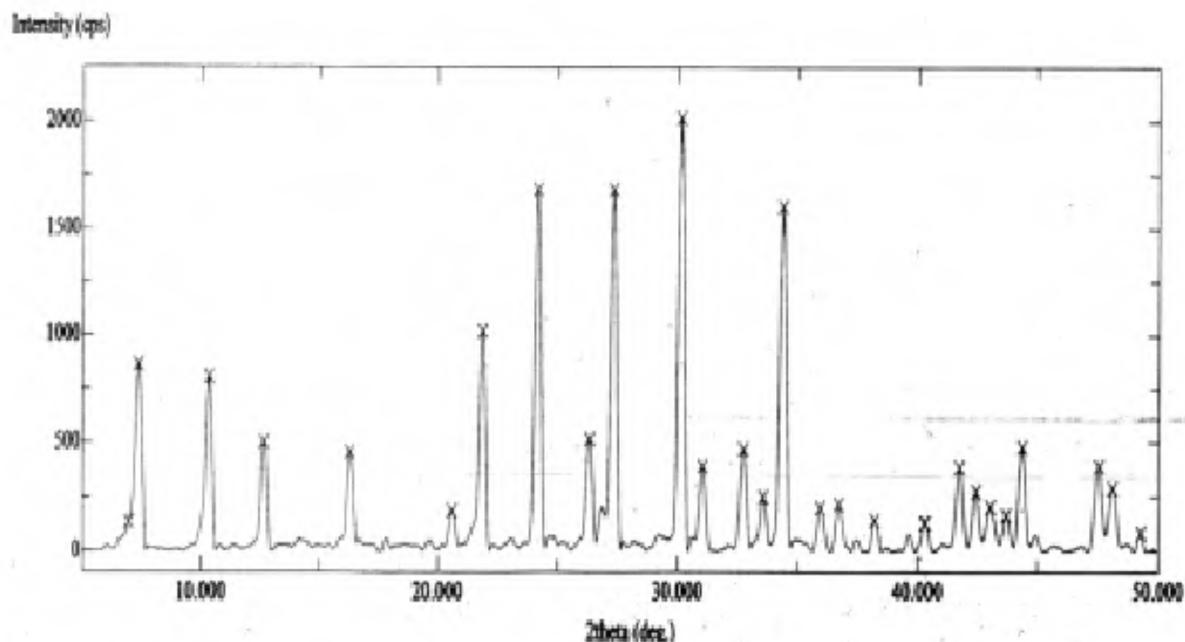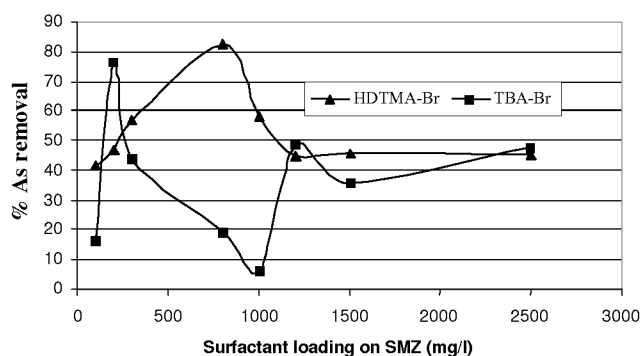**Figure 1.** IR spectra of (*a*) FAZ-A, (*b*) SMZ-A and (*c*) HDTMA–Br.

Figure 2. XRD of SMZ-A.

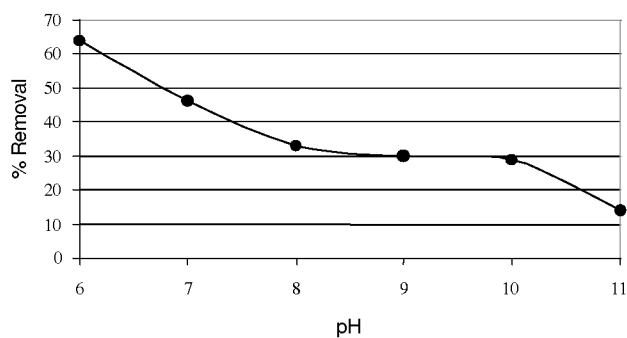**Figure 3.** Effect of loading of surface modifiers (HDTMA–Br and TBA–Br) for As removal.
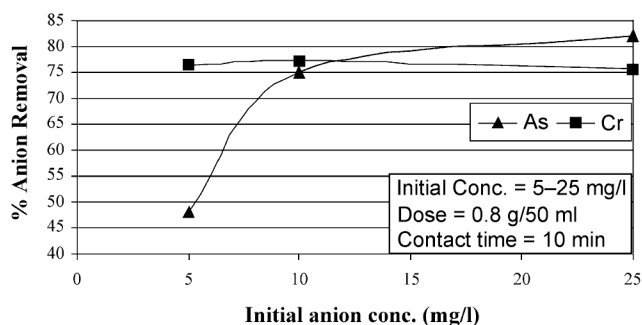

Figure 4. Effect of anion concentration in the initial solution on percentage anion removal.

TBA–Br. When zeolite is treated with high concentration of HDTMA–Br, it exists as a micelle with the hydrophobic end facing outwards; these micelles have lesser affinity for water than the zeolite surface and therefore get adsorbed.

Figure 5. Effect of pH on percentage chromate removal.

These micelles then rearrange to form well-defined bilayers on the zeolite surface. When zeolite-A is treated with these surfactants, at low concentration they form a monolayer on the zeolite surface. HDTMA–Br being more hydrophobic, has more affinity for getting adsorbed. The higher hydrophobicity of HDTMA–Br seems to be the reason for its lower affinity for water and higher affinity for zeolite surface.

Effect of initial As and Cr concentration on per cent anion removal was studied keeping SMZ dose at 0.8 g/50 ml for contact time of 10 min and varying initial anion concentration at 5, 10 and 25 mg/l. It is shown in Figure 4 that the percentage removal increased with increasing As concentration in the initial solution, whereas a different trend was observed for Cr. The removal efficiency was independent of initial concentration under the experimental conditions studied. It was about 75–77%. The removal of oxyanions from aqueous solution is probably taking place
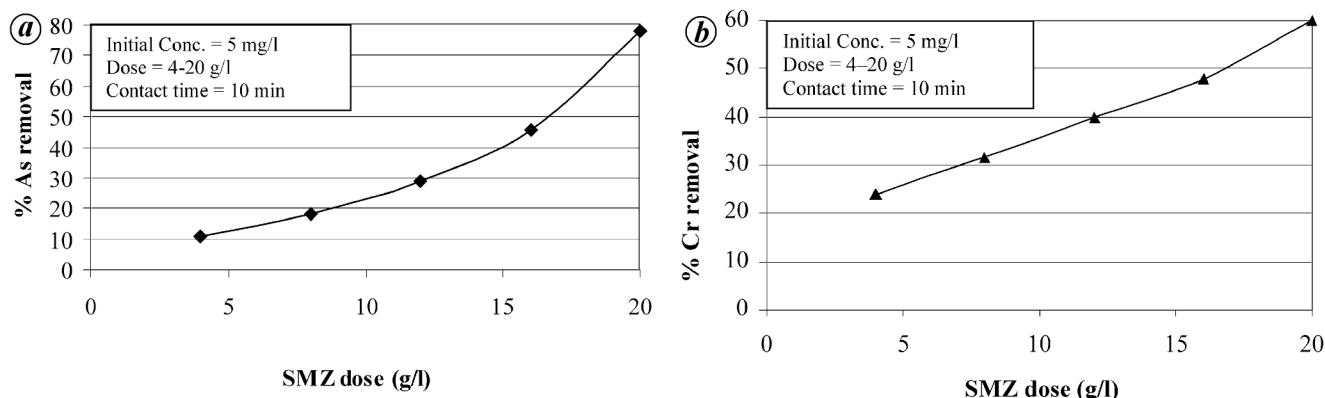
Figure 6. Effect of SMZ dose on (*a*) As and (*b*) Cr removal.

by anion exchange mechanism and the trend corroborates with that reported in the literature. In a study by Li and Bowman[1], HDTMA–Br modified zeolite was found to be more selective for chromium than arsenic and the removal mechanism proposed was ion exchange. The lower selectivity for arsenic was attributed to probable competition from OH^- for adsorption sites.

Effect of pH on anion removal was studied with chromate concentration fixed at 14.85 mg/l, contact time of 30 min, initial concentration of 50 mg/l and dose at 0.5 g/25 ml (Figure 5). The effect of pH below 6.0 was not studied as zeolite is not stable under acidic conditions. Maximum removal efficiency was observed at pH 6.0. Increasing the pH resulted in substantial decrease in removal efficiency for anions. Increasing pH probably results in competition between OH^- ions and chromate. This leads to decrease in its adsorption capacity for anions.

Figure 6*a* and *b* shows the effect of SMZ dose on As and Cr removal respectively, which increases with increasing SMZ dose. A linear relationship has been observed for removal of arsenate and chromate with respect to SMZ dose.

The SMZ described here overcomes the drawbacks of the commercial zeolite-A, which include lack of affinity for arsenic at low concentrations and also lack of versatility for sorption of pollutants ranging from cationic to anionic.

In addition, it offers the following advantages over the conventional methods in vogue:

(i)   Disposal problem by virtue of its possible conversion to value-added ceramic precursors by heat treatment.

(ii) Stabilization of arsenic by pore blocking (unpublished data).

(iii) Cost-effectiveness compared to other adsorbents, by offering a single unit for a wide array of pollutants vis-à-vis multiple units required for targetting a wide array of pollutants.

(iv) Sludge generation associated with conventional chemical method, viz. alum treatment, chemical precipitation, etc.

(v)   Hazardous chemical handling by providing a technically non-tedious and clean process.

The materials designed herein appear to be promising for arsenic as well as chromium removal. The initial concentration of As has reduced from 1.15 to 0.203 mg/l, indicating that it may be a promising material for reducing removal of As below 5 ppb.

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