the same method of analysis, he determined that while the %P in the metal of Delhi pillar was 0.18 (in solid solution), the same in the rust of the Delhi pillar was 0.35%. Therefore, although there was P enrichment in both the rusts, higher amount of P in the Delhi pillar iron resulted in a higher P content in the rust of the pillar.

It is important to note that sufficient atmospheric exposure is required before a uniform protective passive film is formed. Short-term immersion testing and polarization studies will not reveal the characteristics of passive film formation on the surface due to atmospheric exposure[11]. The kinetics of the protective passive film formation on the Delhi pillar has been analysed recently, by considering the known thickness of the protective passive film on the surface and visual observation of protective passive film growth on the surface[23]. It has been concluded that approximately three years will be required for the initial formation of the protective film. Once the protective passive film forms, it grows and covers the surface, and the underlying microstructural variations may be of no consequence. This conclusion is also in agreement with well-established science that surface-sensitive properties like general corrosion and passive film formation in ambient temperature aqueous corrosion or protective oxide formation in high-temperature oxidizing conditions are significantly dependent on the composition of the underlying material, with the material microstructures generally playing only a minor role[24,25].

In summary, the microstructural and compositional inhomogeneities of the Delhi pillar iron do not have any influence on the protective passive film that forms on the surface. The deciding factor that is important in imparting the excellent corrosion resistance is the high P content of the Delhi pillar iron.

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Photocatalytic oxidation of As(III) to As(V) in aqueous solutions: A low cost pre-oxidative treatment for total removal of arsenic from water

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Nonionic nature of As(III) in aqueous solutions, pH less than nine makes it a difficult form of arsenic which cannot be efficiently removed from drinking water by conventional ion exchange and adsorption chromatographic techniques. In the presence of TiO_2 photocatalyst and UV radiation, nonionic H_3AsO_3 can be readily oxidized to the anionic form of As(V) with no formation of metallic arsenic. The rate of oxidation is found to be less pH dependent. The suggested mechanism for the holes and electrons consuming steps are: $H_3AsO_3 + 2h^+ + 4OH^- \rightarrow HAsO_4^{2-} + 3H_2O$ and $2H^+ + 2O_2 + 2e^- \rightarrow H_2O + 3/2O_2$ respectively.

HETEROGENEOUS photocatalytic mineralization has been studied extensively by many research workers as a non-toxic purification technique for water contaminated with heavy metals and organic pollutants[1–3]. Removal of heavy metal pollutants such as mercury[4] is based on photocatalytic reduction with the deposition of metallic

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mercury onto colloidal TiO_2 particle. However, no such method has been cited in the literature for the removal of arsenic.

Conventional purification methods such as anion exchange, membrane-filtration and adsorption techniques require ionic forms of arsenic for the effective removal. Therefore, for total removal of arsenic from water, arsenite [As(III)] must be oxidized to arsenate [As(V)] through a pre-treatment process, which involves addition of oxidizing chemicals. The reason is that arsenite occurs as uncharged arsenious acid (H_3AsO_3) in natural waters having pH less than nine. Only at pH values higher than its $pK_a = 9.2$, arsenite occurs as monovalent ansenite anion ($H_2AsO_3^-$). On the other hand, arsenate, i.e. As(V) occurs as anionic $HAsO_4^{2-}$ in natural waters, which can be removed by conventional adsorption or anion exchange column techniques with a greater efficiency. Previous studies have shown that bubbling of pure oxygen even for a period of an hour could not oxidize As(III) to As(V) under normal conditions[5]. This makes much toxic arsenite a difficult form of arsenic that cannot be removed from water so effectively. It has also been reported[6,7] that some parts of the world (e.g. Bangladesh/India border region) contain high levels of arsenic in waters, well above the limit of 5 $\mu g/dm^3$ recommended by the World Health Organization (WHO). The problem becomes more serious as the nonionic arsenite levels are high in deep well waters under anaerobic conditions[8]. Hence, a low cost method for the removal of total arsenic from drinking water has become an urgent requirement.

In this study we have found that in the presence of colloidal TiO_2 photocatalyst and UV radiation (or Sunlight), As(III) can be readily converted to As(V) within a short period of time, with no concomitant reduction of As(III) to metallic arsenic. As a low cost, non-toxic method for pre-oxidation of arsenite to arsenate, our findings certainly have some practical applications.

TiO_2 and Na_2HAsO_4 were purchased from BDH Chemicals and used without any further purification. Double distilled deionized water was used for all the experiments. Stock solutions of As(III) were prepared by dissolving As_2O_3 (BDH Chemicals) in minimum amount of 20% NaOH and adding deionized double distilled water. Required pH was adjusted[9] by adding 5 M H_2SO_4. Working pH of solutions were maintained at seven except for the study of pH effect on irradiation. 250 W, medium pressure mercury arc discharge lamp was used as the source of UV radiation[4]. Pyrex reaction vessel filtered out excitation light having wavelengths < 300 nm. Weighed quantities of TiO_2 (0.25 g l^{-1}) were dispersed in solutions by sonication ca. 30 min until the particle size distribution remains independent of the sonication time[4]. Depletion of arsenite level with time was monitored by withdrawing samples from the reaction vessel and reacting with excess periodate in acidic medium (pH = 1). pH was adjusted by adding concentrated H_2SO_4. Liberated I_2

was immediately extracted into a hexane layer and absorbance of I_2 was measured at 520 nm[10] using a Cecil UV 2000 series single beam spectrophotometer. Using a calibration curve (i.e. absorbance vs. content of As(III)), variation of As(III) concentration was estimated. Time variation of concentration of As(V) was monitored by withdrawing samples out of the reaction vessel and titrating with 1×10^{-3} M sodium thiosulphate solution[11].

An atomic absorption spectrophotometer, GBC Scientific Equipment (Model 932 G plus) with Hydride Generation System (HG 3000) and Graphite Furnace (GF 3000) were also used to estimate arsenic levels.

Figure 1 b shows the depletion of 100 ppm As(III) level with the time exposure to UV radiation in the presence of colloidal TiO_2 photocatalyst. Inset in Figure 1 shows the rate of depletion when exposed to afternoon sunlight. In the case of sunlight experiments, tenfold excess of colloidal TiO_2 was used to speed up the rate of depletion of As(III) level. Bubbling of air during irradiation does show slightly enhanced rate for the arsenite depletion (Figure 1 a). Control experiments are carried out maintaining identical conditions except with no UV light, but with bubbling air (Figure 1 c) and without bubbling air (Figure 1 d) did not show any significant decrease of As(III) level with time. pH of irradiated solutions was maintained at seven since any practical ap-
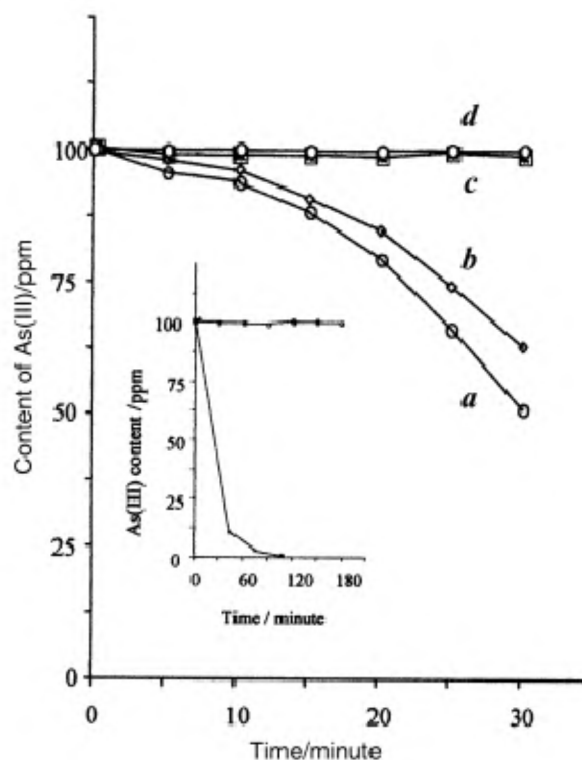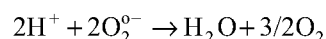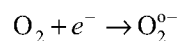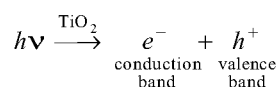

Figure 1. Variation of content of As(III) with time of exposure to UV radiation in the presence, 0.25 g l^{-1} of TiO_2 (a) with bubbling, (b) without bubbling of air, (c) and (d) are respective control experiments without UV radiation at pH = 7. *Inset*: Variation when exposed to sunlight in the presence of 2.5 g l^{-1} of TiO_2.

plication had to be carried out at neutral conditions. Results show that within 60 to 90 min of UV exposure time, more than 80% of arsenite could be converted to another oxidation state, most likely to the As(V) or/and As(0). Independent experiments carried out for the determination of As(III) levels using atomic absorption measurements (hydride generation) also confirmed that As(III) content decreases with the exposure time to UV radiation in the presence of colloidal TiO_2 particles.

Figure 2 shows the variation of concentration of As(V) with time for the air-purged solutions when exposed to UV radiation in the presence of colloidal TiO_2 and its control experiments, i.e. maintaining identical experimental conditions, but without UV radiation. It shows that As(V) content increases with the UV exposure time and remains almost constant in the control experiment. It is clear that some amount of arsenite has been converted to arsenate when exposed to UV radiation in the presence of a photocatalyst. Interestingly, experiments carried out to determine variation of total arsenic [i.e. As(III) + As(V)] level during irradiation, using furnace atomic absorption technique indicated that total As level remains unchanged with an approximate variation of 110 ± 15 ppm. These results clearly suggest that in the presence of colloidal TiO_2 and UV irradiation, arsenite converts to arsenate. Bubbling air during irradiation does show enhanced rate for the depletion. The increase in the rate could be due to the efficient acceptance of photogenerated electron by the dissolved oxygen in the solution. The arsenite depletion rate may increase by direct attack of species like superoxide and hydrogen peroxide formed in the presence of dissolved oxygen. Experiments carried

out under different pH conditions, ranging from 1 to 13 indicate that arsenite depletion rate is less pH dependent. Addition of EDTA or citric acid, which could act as a sacrificial oxidizing and complexing agent does not show any enhancement for the rate of As(III) depletion. However, addition of citric acid can act as buffering agent, which could be used to keep the solution at constant pH value. When N_2 was purged in place of air through the sample during UV irradiation, rate of depletion of As(III) drops appreciably, suggesting that dissolved oxygen plays an important role in the photocatalytic mechanism.

The suggested mechanism for the electron and hole consumption processes is:

$$h\nu \xrightarrow{\text{TiO}_2} \underset{\substack{\text{conduction} \\ \text{band}}}{e^-} + \underset{\substack{\text{valence} \\ \text{band}}}{h^+}$$

$$H_3AsO_3 + 2h^+ + 4OH^- \rightarrow HAsO_4^{2-} + 3H_2O$$

$$O_2 + e^- \rightarrow O_2^{o-}$$

$$2H^+ + 2O_2^{o-} \rightarrow H_2O + 3/2 O_2$$

It is noteworthy that arsenate [As(V)] does not show any photocatalytic reduction or oxidation and remains as arsenate. This is not surprising, as the photo-reduction of negatively charged arsenate is highly unlikely by electron in the conduction band. Photo-oxidation of As(V) to higher oxidation levels by generated hole in the valence band is also thermodynamically unfavourable.
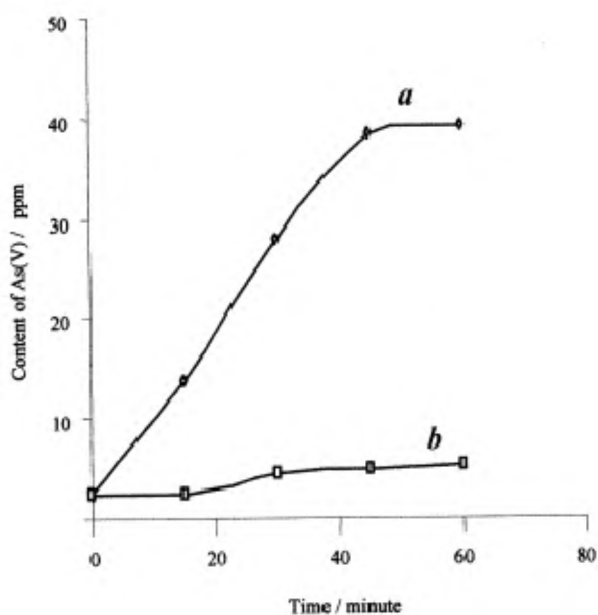
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Figure 2. Time variation of As(V) content in the presence 0.25 gl^{-1} of TiO_2: (*a*) when exposed to UV radiation and (*b*) corresponding control experiment without UV radiation. Samples were bubbled with air during UV exposure time. Working pH = 7.