

Adsorption of arsenic (V) and arsenic (III) onto different uncalcined and calcined aluminium hydroxide powder

I.N. Bhattacharya^{1,*}, P.K. Gochhayat¹, S. Paul², P.K. Mitra²

¹ Regional Research Laboratory, Bhubaneswar, Orissa, India

² Department of Metallurgy, Jadavpur University, Kolkata-700032, India

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ABSTRACT

Fine (1.5 μm) and coarse (~100 μm) aluminium trihydroxide (ATH), gibbsitic in nature and low bulk density (0.3g/cm³) gel aluminium hydroxides (basic aluminium sulfate, BAS) were used as precursor material for obtaining various calcined products at different temperatures up to 1200°C. These calcined products were used for adsorption of As(III) and As(V) from aqueous media. As(III) and As(V) adsorptions were found effective for fine gibbsitic materials calcined at 350°C and for coarse gibbsite particles calcined at 400°C. Similarly low bulk density BAS calcined at different temperatures up to 900°C showed high adsorbability for As(V) but As(III) separation was not effective. Gibbsite when heated between 350-400°C transformed to boehmite while low bulk density BAS remained amorphous up to 800°C and at 900°C it transformed to η -alumina. It was found that chi and kappa forms of transition aluminas formed by calcining gibbsite at 500°C and 1000°C respectively showed lower adsorption efficiencies than boehmite phase. The α -alumina obtained from different sources showed different adsorbability for As(V) and As(III). Variation of temperature and pH showed dependency of adsorbability on such parameters. It was found further that degree of dehydroxylation had effect on the adsorbability. Total dehydroxylation such as in the case of α -alumina, had no or less activity. Surface area showed beneficial effect on adsorption. The crystalline phase, extent of dehydroxylation and desulfurisation, surface area, starting precursor etc., were found to have bearing on adsorption efficiency of a material. The As(III) adsorption showed major dependency on surface area but As(V) adsorption showed combined dependency on above parameters. © 2005 SDU. All rights reserved.

Keywords: Arsenic; Adsorption; η – alumina; Boehmite; Gibbsite; Transitional alumina

1. INTRODUCTION

Naturally occurring arsenic in ground water is one of the most toxic pollutants to humans (Saha *et al.*, 1999). Recently it created serious health problem in various parts of the globe (Chakraborty *et al.*, 1998; Vogels *et al.*, 1998; Smedly *et al.*, 2000). The arsenic concentration in ground water is found to be between 0.5ppb to 5ppm (Smedly *et al.*, 2000). The consumption limit of arsenic was fixed by WHO (World Health Organisation) as maximum of 0.05ppm but subsequently in many countries the limit has been revised to 0.01ppm. Arsenic in ground water is found in inorganic form as oxyanions of trivalent arsenite and pentavalent arsenate. In many cases as arsenite is difficult to remove, oxidation is performed (Harris, 2000; Shen, 1973) to transform to arsenate and then it is removed. But this oxidation process becomes very expensive in many occasions. There are various technologies (Hopkin, 1988; Robins, 1988; Robinson *et al.*, 1994; Robins *et al.*, 1998; Vogels *et al.*, 1998) available for removal of arsenic from ground water or from industrial effluents.

The various separation processes available today are oxidation-reduction, precipitation, co-precipitation, electrolysis, solvent extraction, ion exchange, membrane separation, etc. (Robins, 1988). Adsorption behaviour of arsenic (III) and arsenic (V) onto activated charcoal was carried out by various authors (Huang *et al.*, 1984; Eguez *et al.*, 1987; Pokonova, 1998). Eguez *et al.* (1987) observed that As(III) adsorption remained constant between pH ranges 0.16 to 3.5, whereas As(V) adsorption showed maximum at pH 2.35. Hydrated titanium dioxide is also used as adsorbent for arsenic removal (Madsen *et al.*, 1983). Adsorption of arsenic oxyanions onto lanthanum oxide was studied by Rawat *et al.* (1998). The results

* Corresponding author. E-mail: inbhattacharya@rllbhu.res.in

showed that temperature had positive influence on the rate and degree of adsorption. The decrease in activation energy with concentration indicated heterogeneous adsorbent surface. Ferric oxy hydroxides (Issacson *et al.*, 1994) were used to remove arsenic from aqueous stream. The treatment reduced the arsenic content below US National Drinking Water Standards. Ion exchange techniques (Fu *et al.*, 1995) were also used to remove arsenic. Hydrous zirconium oxide (Suzuki *et al.*, 2001) was also used for arsenic removal. Trace levels of As(III) and (V) in aqueous media were effectively adsorbed on to a coral limestone loaded by Fe(OH)₃ (Maeda *et al.*, 1990; Maeda *et al.*, 1992). It was found that both arsenic (III) and (V) adsorptions are comparable. Adsorption was independent of pH in the range 3 to 10 for arsenic (III) and 2 to 10 for arsenic (V). Adsorption isotherm for both (III) and (V) variety followed Freundlich isothermal relationship. In CRC-ANSTO process (Khoe *et al.*, 1999), light and iron salt was used to accelerate the arsenic oxidation reaction with air. The added iron was also used as a precipitant for arsenic removal. The co-precipitated arsenic is settled and removed with iron hydroxide sludge. They have been successful in reducing the arsenic contamination to less than 0.05ppm. Vogels and Johnson (1998) developed an efficient method for removal of arsenate and arsenite from drinking waters using ferrate and ferrous ions. This process has been successful in bringing down the arsenic concentration to below 5ppb. Clifford (1990) reports both anion exchange and activated alumina adsorption techniques for arsenic removal. Which are in use for drinking water purpose. Alumina adsorption is specific for arsenate and not influenced by dissolved solids (TDS). Ramana and Sengupta (1992) stressed the need to adjust pH below 6 for arsenic adsorption onto activated alumina. Kahelin *et al.* (1998) tested chemical coagulation, ion exchange adsorption process and membrane separation for arsenic removal. The processes were tested by oxidizing arsenic (III) to arsenic (V). The three household water treatment facilities tested were based on activated carbon, activated alumina and ion exchange. Activated alumina was found to be most successful than other two and activated carbon gave the poorest results. In aqueous systems arsenic exhibits anionic behaviour and behaves like ligands in water. Ferguson and Anderson (1974) found sorption of arsenic on iron and aluminium hydroxide to follow Langmuir isotherm. Arsenite is less strongly sorbed on the same material and varied linearly with concentration. Various authors (Anderson *et al.*, 1976; Gupta *et al.*, 1978; Pierce *et al.*, 1980) showed that sorption of As(III) onto alumina decreased at pH above 9, while that of As(V), it decreased when pH is above 7. Ghosh *et al.* (1987) showed adsorption of As(III) onto activated alumina was greatly dependent on pH.

As discussed above adsorption process is found to be one of the most successful processes for removal of arsenic. The removal of arsenic through activated alumina has long been practiced as an effective means. Use of alumina over others as adsorbent has various advantages, such as they do not swell, and have crushing strength, abrasive resistance and negligible solubility in water. They are also very good in removing trace quantities and very selective (Wefers *et al.*, 1987). It has been proved that adsorption of a particular material depends mainly on the morphology and synthesis methodology (Wefers *et al.*, 1987; Fleming, 1990; Fleming *et al.*, 1990). The surface properties of adsorbent mainly indicate its applicability. The transitional aluminas are most suitable for such adsorption purpose. These aluminas possess surface hydroxyls, which have certain degree of activity in adsorption (Wefers *et al.*, 1987; Fleming *et al.*, 1990). The loss of hydroxyl ions results in defect structure in Al and O₂ lattice (Wefers *et al.*, 1987; Fleming, 1990; Fleming *et al.*, 1990). The α -alumina, aluminium hydroxides or stable oxyhydroxides are not very effective because they have very less porosity, lower surface area, almost total dehydroxylation and have no defect structure. As stated the hydroxyls exhibit various functionalities ranging from very basic to partially acidic (Wefers *et al.*, 1987; Fleming *et al.*, 1990). Cornelius *et al.* (1955) suggested "strained" oxygen bridges, resulting from the condensation of two adjacent hydroxyl ions, to be the catalytically active sites. Excessive condensation of adjacent OH⁻ ions creates local disorder; at around 90% removal of hydroxyl ions, no pair of neighbouring OH⁻ ions is left (Peri, 1965). Surface migration of protons or hydroxyl ions is required for any additional dehydroxylation. This situation shows probably the greatest catalytic activity. Adsorption process in aqueous system follows mainly three mechanisms (Fleming, 1990). Adsorbing species can chemisorb and forms a surface complex via co-valent bonding to the aluminium. In second mechanism electrostatic charge derived by surface protonation. The third mechanism of adsorption with alumina is through ion-exchange, which occurs via surface protons and hydroxyls.

In the present study adsorptions of As(V) and As(III) were taken up with three different aluminium hydroxide materials. These aluminium hydroxides were calcined at various temperatures up to 1200°C to obtain activated alumina of different grades. The materials taken for the study were i) fine aluminium trihydroxide (gibbsite, 1.5 μ m) precipitated from plant Bayer liquor by adding grain refining modifier and ground seed (Pradhan *et al.*, 2001; Bhattacharya *et al.*, 2002), ii) coarse ATH (~100 μ m) obtained from M/s Nalco, India and iii) low bulk density (0.3g/cm³) gel aluminium hydroxide (Bhattacharya *et al.*, 2004b) known as basic aluminium sulfate (BAS) obtained through hydrolysis of aluminium sulfate with ammonia. In this study fine material was taken to find out its suitability as adsorbent over coarse variety. The low bulk density gel aluminium hydroxide was also investigated for its suitability as adsorbent. As a whole the major

aim was to correlate various characteristic features of different uncalcined and calcined products with As(V) and (III) adsorptions.

2. EXPERIMENTAL

The precipitated fine ATH and low bulk density aluminium hydroxides used in this study were prepared through an indigenously developed process mentioned earlier. Different calcined products were prepared by heating fine and coarse gibbsite and low bulk density gel (BAS) at different temperatures up to about 1200°C for 2h. While heating various phase changes occurred which are mentioned in the characterization of material portion and also reported elsewhere (Wefers *et al.*, 1987; Bhattacharya *et al.*, 2004a,b).

2.1. Adsorption of arsenic

Arsenic (V) standard solution of 1000ppm was obtained from E.Mark, 6427 1, Damstadt West Germany. Arsenic (III) solution of 1000ppm strength was prepared from analytical grade reagent of AJAX Chemicals, Sydney, Australia by dissolving the solid arsenic oxide in distilled water with controlled addition of dilute NaOH (~0.1M) solution. Stock solutions were utilized for preparation of different concentration of arsenic solution as required in the experiment. The majority of the adsorption work was carried out with As(V) and few experiments with arsenic (III) to know the adsorbents ability to remove As(III). The analysis of As(V) was carried out by standard molybdenum blue method (Vogel, 1978; Roy *et al.*, 1979). Arsenic (III) was analysed by oxidizing (III) to (V) by adding KMnO₄ and then following As(V) method. Optical density of arsenic solution was measured in a Varian (model) UV spectrophotometer.

The adsorption of arsenic onto uncalcined and calcined powders was carried out in a glass vessel of 250ml/500ml capacity covered with a lid. The lid had provision for inserting the stirring rod and an opening for sampling. A known volume of arsenic aqueous solution was placed in the reactor and a known quantity of adsorbents was added to it. The adsorbent particles were kept suspended by slow agitation (~50-75rpm) through a Remi make variable speed stirrer. The suspension of particles was easy because the particles are fine and light. In case of coarser size particles higher agitation speed (~250) was maintained. Depending upon the experimental requirements 50ml/100ml/150ml aqueous arsenic solutions were used in the study. The samples were collected at regular intervals. The sampling of arsenic solution was carried out by taking out around 20ml of solution each time with adsorbent through a pipette and filtering it in Sartorius make cellulose nitrate filter. 0.8µm and 1.2µm pore size filter papers were used for filtering fine ATH and low bulk density BAS powders respectively. For coarser particles standard whatman filter paper no.1 was used. After filtration filtrate was analyzed for As(III) or As(V) as required.

Various other experimental conditions used are shown in respective figures. The temperature (wherever required) was maintained by a Julabo make constant temperature bath. All other experiments were carried out at 30°C. pH of the solution was varied by adding NaOH or H₂SO₄.

2.2. Determination of adsorption efficiency

Adsorption efficiency of adsorbents was calculated by analyzing the original solution and the filtrate after adsorption as follows

$$\frac{\text{Original arsenic concn. in solution} - \text{Arsenic concn. in solution after adsorption}}{\text{Original arsenic concentration}} \times 100\% \quad (1)$$

2.3. Determination of adsorption capacity

Adsorption capacity, mg/g, is calculated as quantity (mg) of arsenic adsorbed from the aqueous phase per g of adsorbent.

$$\text{Adsorption capacity} = \frac{\text{Arsenic adsorbed (mg)}}{\text{Quantity of adsorbent (g)}} \quad (2)$$

2.4. Instrumental technique used

BET surface areas of uncalcined and calcined powders were measured in a Quantasorb equipment of quantachrom, USA.

2.5. Characterisation of material

Both the fine gibbsite (1.5 μm) and the coarse gibbsite ($\sim 100\mu\text{m}$) are crystalline material. Fine variety is used in non-metallurgical areas and coarse is used for production of metal. On heating at various temperatures both fine and coarse gibbsite transformed to various transitional phases before becoming stable α -alumina. The various phase transformations occurred are as follows, at 300-400 $^{\circ}\text{C}$, boehmite phase ($\gamma\text{-AlOOH}$) is formed, at 500 $^{\circ}\text{C}$ a transitional chi-alumina is obtained, on further heating at 900-1000 $^{\circ}\text{C}$, kappa-alumina is formed and at 1200 $^{\circ}\text{C}$ to 1400 $^{\circ}\text{C}$ most stable α -alumina is obtained. These phase transformations are given elsewhere (Bhattacharya *et al.*, 2004a). Low bulk density aluminium hydroxide (BAS) contains water of hydration and sulfates in the structure. This powder as mentioned is amorphous in nature and forms η -alumina on heating at 900 $^{\circ}\text{C}$. Stable α -alumina from these precursor materials was obtained by heating at 1100-1200 $^{\circ}\text{C}$.

3. RESULTS AND DISCUSSION

The majority of adsorption tests were carried out at pH 6.9 except where pH variation was made. Similarly temperature was maintained mostly at ambient conditions (30 $^{\circ}\text{C}$) other than where temperature was varied. In this study as mentioned earlier three different materials were taken. Fine and coarse gibbsite particles are crystalline in nature and the other variety is an amorphous material.

3.1. Adsorption of arsenic (V)

3.1.1. Adsorption of As(V) onto fine ATH (gibbsite) powder

Figure 1 shows the adsorption of arsenic (V) onto precipitated fine gibbsite powder and its calcined products as a function of calcination temperature. Adsorption efficiency was shown after 60 minutes of contact time. In these experiments a comparison was made between different calcined products to find the optimum calcination temperature for maximum adsorption. Uncalcined fine gibbsite showed very poor adsorption capacity (23%), whereas fine gibbsitic material calcined at 350 $^{\circ}\text{C}$ showed maximum adsorption of 92% at 60 min. time. The 1200 $^{\circ}\text{C}$ calcined material showed no adsorption at all. It is known (Wefers *et al.*, 1987; Fleming, 1990; Fleming *et al.*, 1990) that adsorption capacity depends on various factors such as, surface area, porosity and surface morphology i.e., degree of dehydroxylation. From Figure 2 it has been observed that the surface area at 350 $^{\circ}\text{C}$ (311 m^2/g) is the maximum whereas at 1200 $^{\circ}\text{C}$ the surface area is only 14 m^2/g , which is even lower than the precipitated uncalcined gibbsite powder (30 m^2/g).

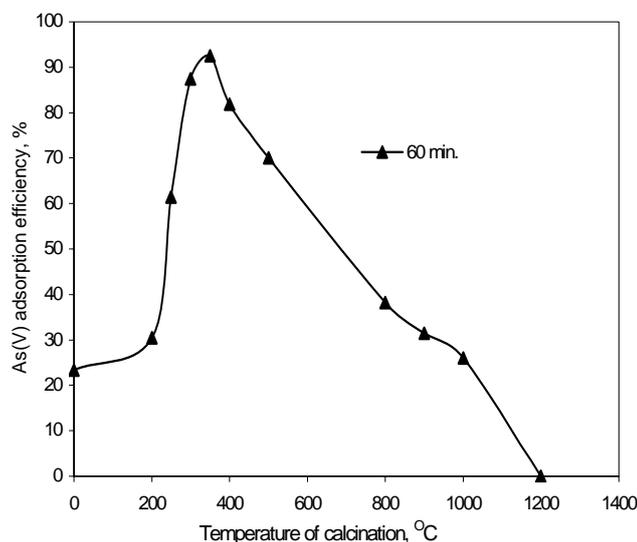


Figure 1. Adsorption of As(V) onto various calcined fine gibbsite as a function of calcination temperature (Adsorbent quantity: 0.5g, As(V): 16.05ppm, Total amount of arsenic in the solution: 1.605mg)

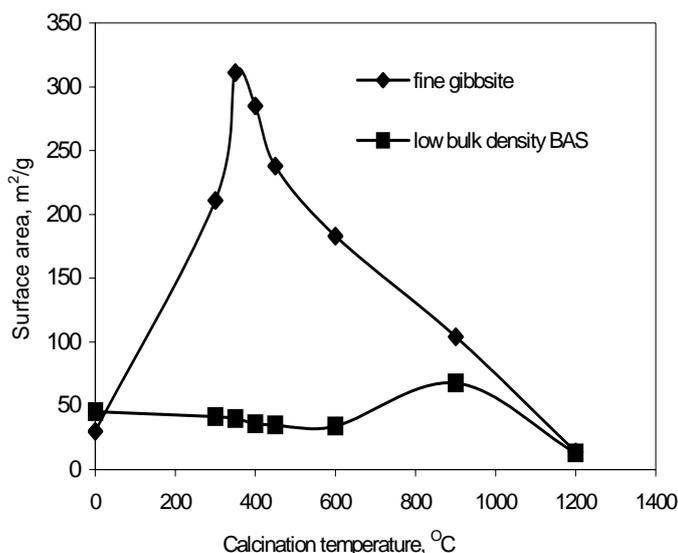


Figure 2. Variation of BET surface area with calcinations temperature for fine gibbsite and low bulk density BAS

The surface area of fine gibbsite material showed initial increase with calcination temperature up to a maximum at 350°C and further decrease in surface area with increase in calcination temperatures beyond 350°C. Similarly adsorption percentage also increased up to a maximum at 350°C calcined product and further reduction in adsorption was observed thereafter and at 1200°C adsorption was found to be zero. This thus indicates adsorption is dependent on surface area. In addition to surface area, degree of dehydroxylation will have influence on adsorption activity. Generally transition aluminas possess good amount of activity as they undergo effective dehydroxylation but α -alumina does not have activity, as it is totally dehydroxylated (Fleming *et al.*, 1990). It was stated earlier that maximum adsorption was achieved for the material calcined at 350°C. The XRD study showed that at this temperature boehmite is the only predominant phase formed. At this temperature around 75-78% dehydroxylation has occurred. The dehydroxylation imparts two fold advantages; it develops active surface hydroxyls and also develops lattice imperfections such as defect structure in Al and O₂ lattice. Excessive dehydroxylation omits such active surface hydroxyls and also lessens lattice imperfections. Similarly low dehydroxylation does not develop active hydroxyls and defect structure. Optimal dehydroxylation is one of the most essential requirements for activity. The transitional phases formed after calcining at 500°C (chi-alumina) and 1000°C (kappa-alumina) are not very effective adsorbent compared to boehmite phase formed at 350°C. Chi-alumina obtained after calcining at 500°C showed 70% adsorption and kappa-alumina obtained after calcining at 1000°C showed only 26% adsorption. This may be due to progressive decrease in surface area with calcination temperature and excessive dehydroxylation. At 500°C, 85% dehydroxylation and at 1000°C, 96% dehydroxylation were observed. In case the adsorption efficiency is solely dependent on surface area a linear correlation is expected between percent adsorption and surface area. But in the present case this was not found. At 300°C, surface area was 211 m²/g and adsorption was 88% whereas at 400°C surface area was 285 m²/g but adsorption was reduced to 81%. Further, at 450°C, surface area was 238 m²/g but adsorption reduced to around 70%. The difference in adsorbability is due to difference in degree of dehydroxylation. At 300°C, degree of dehydroxylation is favourable for adsorption of arsenic than 400°C or 450°C. From this it has been observed that the optimum combination of surface area, dehydroxylation and the crystalline phase are responsible for surface activity.

Figure 3 shows adsorption kinetics of arsenic (V) at different adsorbent quantity for 350°C calcined material. Adsorption efficiency was increased with adsorbent quantity. The adsorption kinetics followed an initial rapid adsorption period and then a slower period. In fact within one minute of adsorption around 70.5% of arsenic was removed for 0.75g adsorbent, 70% for 0.65g adsorbent, 66% for 0.55g adsorbent and 52% for 0.45g adsorbent. But after 3h of adsorption more than 90% adsorption was found in all the cases, and maximum (~97%) being with 0.75g of adsorbent. Effect of temperature on adsorption (Figure 4) of As(V) showed progressive increase in adsorption with temperature. Increase in temperature appeared to improve initial rate and degree of adsorption. At 48°C, 100% removal of As(V) was observed. At 40°C and 45°C around 96% adsorption was found. Figure 5 indicates the effect of pH on As(V) adsorption. The arsenic adsorption remained almost unaffected up to pH of around 9.15 but beyond this pH it decreased considerably and no adsorption at pH around 12.

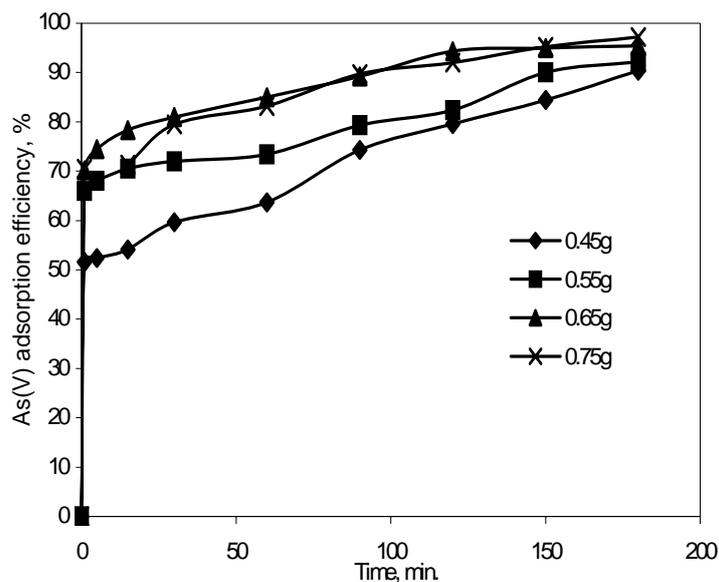


Figure 3. Adsorption of As(V) onto 350°C calcined fine gibbsite powder at different adsorbent quantity as a function of time (As(V) – 12.2ppm, 1.83mg)

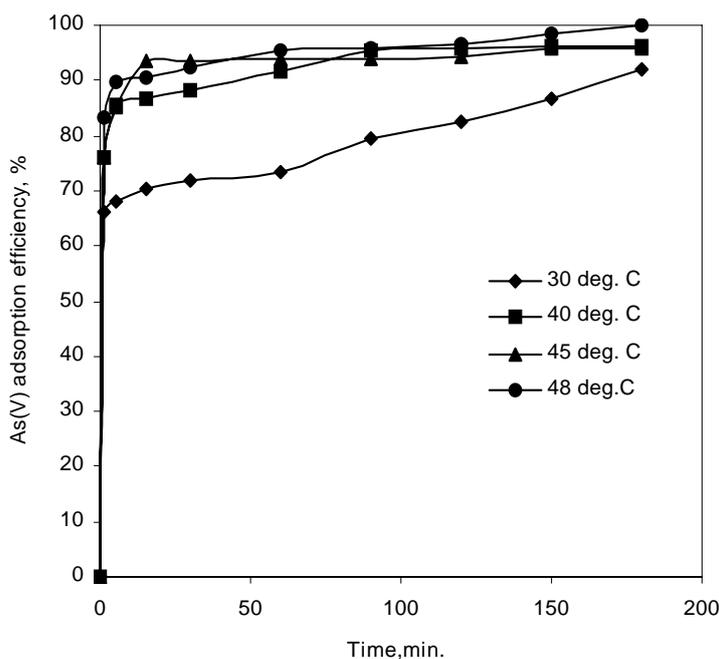


Figure 4. Adsorption of As(V) onto 350°C calcined gibbsite powder at different temperatures as a function of time (Adsorbent quantity-0.55g, As(V)- 12.2ppm, 1.83mg)

Figure 6 shows the adsorption capacity (arsenic adsorbed in mg per g of adsorbent) of arsenic onto fine boehmite (calcined at 350°C) as a function of both temperature and adsorbent quantity. It has been observed that with increase in temperature, adsorption capacity has increased which followed the predicted line. But in case of adsorbent quantity, the adsorption capacity decreased with increase in adsorbent quantity. It therefore indicate that adsorption of As(V) is not proportional to the available surface area or the heterogeneous nature of the adsorbent surface.

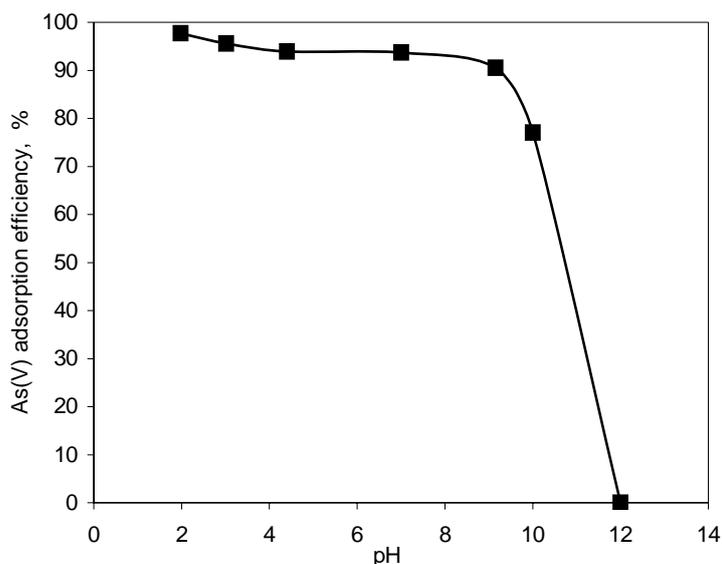


Figure 5. Effect of pH on adsorption of As(V) onto 350°C calcined fine gibbsite (boehmite) powder (Adsorbent quantity-0.2g, As(V)- 12.2ppm, 0.61mg)

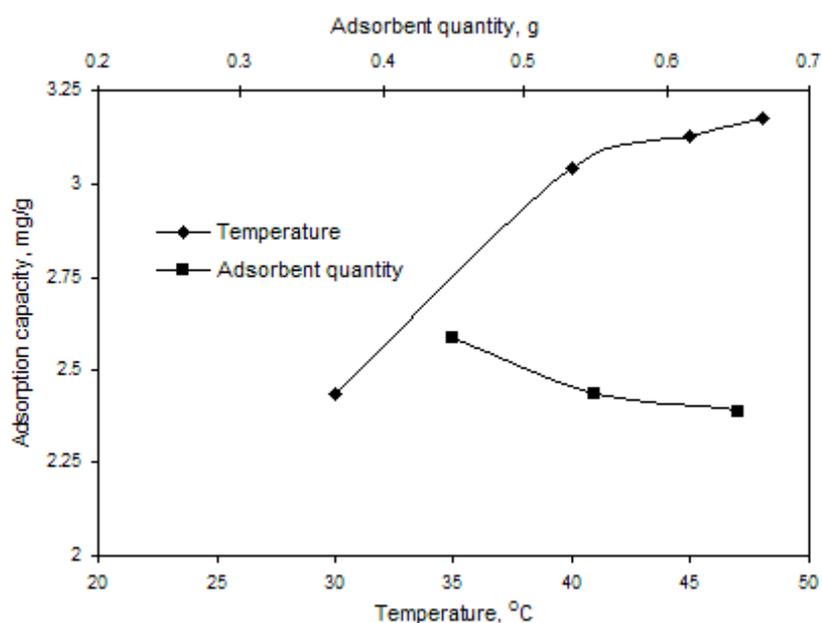


Figure 6. As(V) adsorption capacity of fine boehmite with adsorption temperature and adsorbent quantity (As(V) - 1.83mg, Adsorbent quantity for temperature curve- 0.55g)

3.1.2. Adsorption of As(V) onto coarse ATH (gibbsite) powder

Coarse gibbsite powders (~100µm) calcined at various temperatures showed (Figure 7) maximum adsorption for 400°C calcined material. At this temperature the calcined product has boehmite structure. At 400°C it showed more than 80% adsorption while at 350°C, it reduced to 67% only. With further increase in calcination temperature beyond 400°C adsorption of arsenic has reduced. The 80% adsorption for coarse boehmite particles compared to that of 92% for fine boehmite might be due to the lower surface area of coarse boehmite. At 400°C, the surface area of coarser particles is 238m²/g, which is much lower than that obtained for the fine boehmite (311m²/g) at 350°C. The surface area of coarser gibbsite at 350°C calcined condition was 171m²/g, which is less than the surface area obtained at 400°C calcined condition. Dehydroxylation for boehmite at 400°C was found to be 75-78%. It has been also observed that adsorption

of As(V) was not appreciable at 500°C (chi-alumina) and at 1000°C (kappa- alumina). No adsorption was found for α -alumina obtained at 1200°C calcined condition.

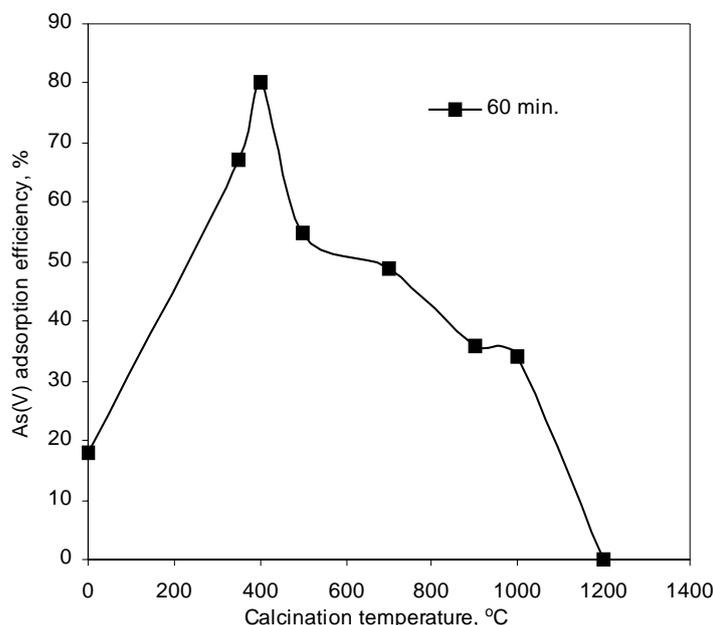


Figure 7. Adsorption of As(V) onto different calcined coarse gibbsite as a function of calcination temperature (Adsorbent Quantity-0.5g, As(V) - 16.05ppm, 1.605mg)

3.1.3. Adsorption of As(V) onto low bulk density gel aluminium hydroxide (BAS) powder

Figure 8 shows the adsorption of As(V) onto precipitated low bulk density BAS powder and its calcined products at various temperatures. It has been found that within 60 minutes 100% arsenic adsorption was achieved for material calcined between 250°C to 350°C and for 900°C calcined materials. A substantial amount of arsenic was adsorbed even with one minute of contact time. Beyond 900°C calcination temperatures percentage of adsorption has dropped and at around 1200°C only 50% adsorption is noticed with 60 minutes of contact time. On the other hand around 98% adsorption is observed for uncalcined material. This BAS powder is amorphous in nature and indifferent to X-ray diffraction. The powder retains its amorphous nature till below 900°C and at 900°C it transforms to a transitional phase alumina known as η -alumina and at 1100-1200°C to α -alumina. It was further found that maximum As(V) adsorption was related to 75-78% dehydroxylation achieved with 350°C calcined material. Similar amount of dehydroxylation was noticed for fine and coarse ATH when heated at 350°C and 400°C, respectively. 100% adsorption observed at 900°C calcined material may be due to the formation of η -alumina. This η -alumina had around 97% dehydroxylation and desulfurisation. In this case also dehydroxylation was 75-78% after deducting desulfurisation portion of about 17-20%. From the Figure 2 it has been found that surface areas of the BAS powders are very low compared to that of fine gibbsite calcined products. Maximum surface area obtained for 900°C calcined material (η -alumina) is 68m²/g. Surface area for uncalcined powder is 45m²/g. At other temperatures surface area has decreased and at 1200°C surface area is only 13m²/g. Increase in surface area at 900°C is due to desulfurisation. Therefore, it has been found that surface area was not the major controlling factor for substantial adsorption in this case, rather surface defects originated in the uncalcined condition, dehydroxylation and desulfurisation etc. contributed mostly. It is very interesting to note that α -alumina obtained through calcinations at 1200°C from gibbsite particles showed no adsorption whereas for α -alumina from BAS showed 50% adsorption. It is therefore proved that starting precursor material has influence on the activity of α -alumina. Figure 9 shows the percentage of arsenic adsorption onto 350°C heat treated material at different adsorption temperatures. Higher temperature favoured higher adsorption as in the case of fine boehmite material. 100% adsorption was noticed when temperature was raised to 48°C with 0.25g of adsorbent. Similarly higher percentage of adsorption was noticed for higher amount of adsorbent (Figure 10). With 0.75g of adsorbent 100% adsorption was noticed within 1 minute of contact time. With 0.65g of adsorbent 100% adsorption was noticed within 30 mins of adsorption and in other two cases maximum adsorption of 95% and 97% was noticed for 0.25g and 0.45g, respectively. It has been observed that within one minute substantial amount

(80-100%) of adsorption was achieved depending upon the quantity of adsorbent. In temperature curves (Figure 9) similar observations were also noticed. It looks; therefore, this material is highly efficient adsorbent for As(V) adsorption. Other interesting observations were noticed when adsorption capacity (adsorption of As(V) in mg per g of adsorbent) was plotted against adsorbent quantity (Figure 11). Adsorption capacity was found to be maximum with low concentration of adsorbent.

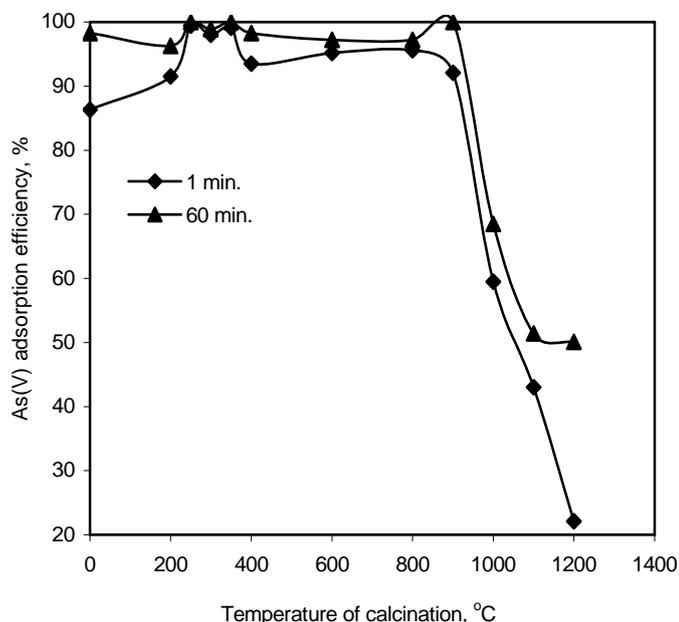


Figure 8. As(V) adsorption onto uncalcined and different calcined low bulk density BAS powders as a function of calcination temperature (Adsorbent Quantity-0.5g, As(V) - 16.05ppm, 1.605mg)

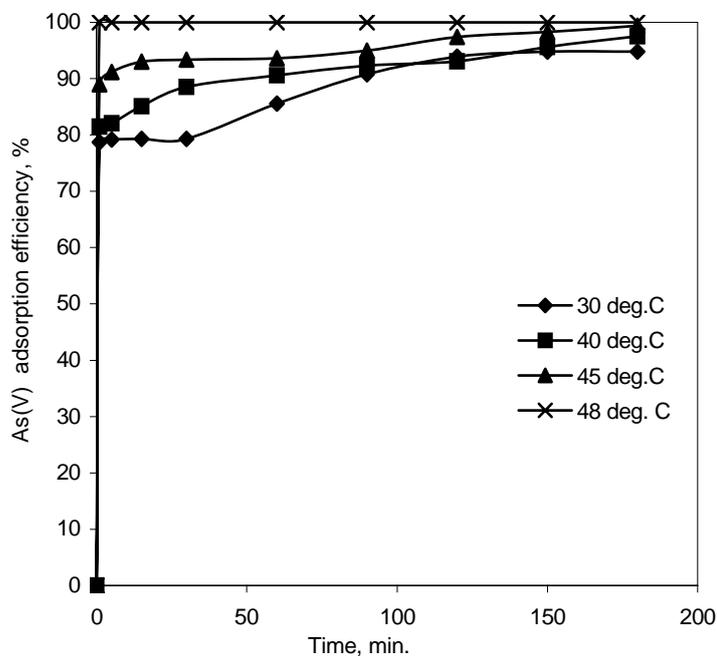


Figure 9. Adsorption of As(V) onto 350°C calcined low bulk density BAS powder as a function of time at various adsorption temperatures (As(V)- 12.2 ppm, 1.83mg, Adsorbent quantity-0.25g)

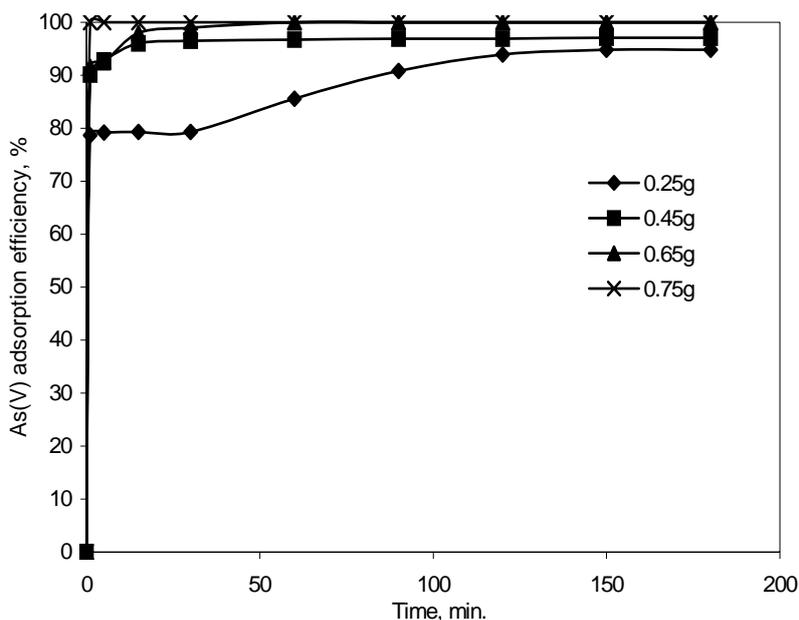


Figure 10. Adsorption of As(V) onto 350°C calcined BAS powder as a function of time at different adsorbent quantity (As(V) - 12.2ppm, 1.83mg)

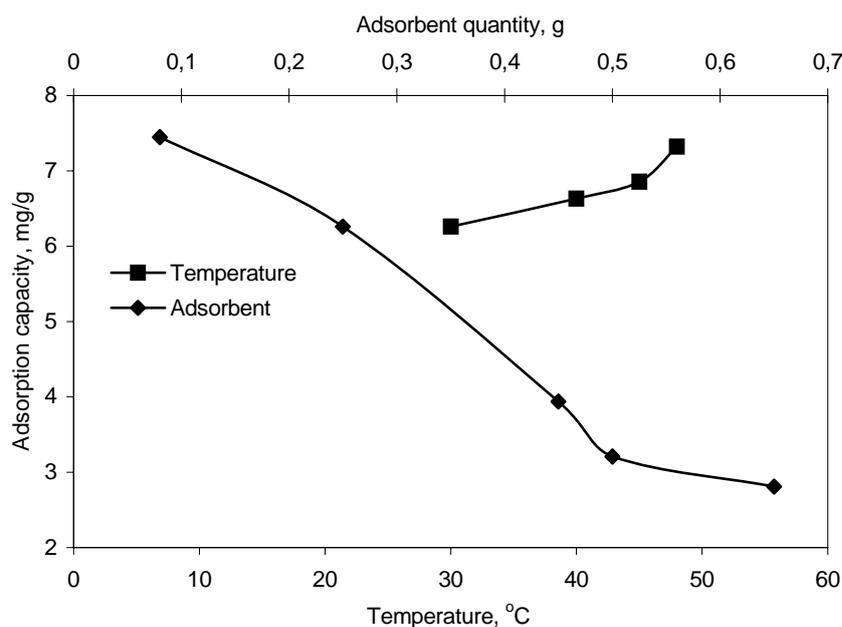


Figure 11. As(V) adsorption capacity of 350°C calcined BAS powder with temperature and adsorbent quantity (Adsorbent quantity for temperature curve - 0.25g)

The adsorption capacity has decreased with adsorbent quantity before becoming almost constant at higher adsorbent concentration. This implies lower arsenic concentration may be effectively adsorbed with lower quantity of adsorbent than adsorbing higher concentration of arsenic with proportionately higher adsorbent quantity. In other way it can be said that same quantity of adsorbent can be used in two or more steps for obtaining enhanced adsorption. Effect of temperature on adsorption capacity is also shown in Figure 11. It has been found that the adsorption capacity has increased with increase in temperature. Both the behaviours are similar to that of fine boehmite. Effect of pH on adsorption of As(V) onto 350°C calcined material showed maximum adsorption at around 9 pH (Figure 12). 100% adsorption noticed at 9.15 pH

within the studied experimental conditions. Adsorption of arsenic (V) is found to be very low in acidic pH range and also very low at higher pH. At around 12 pH no adsorption was found, which is similar to fine boehmite case. But in case of fine boehmite adsorption was almost unaffected up to around 9 pH but beyond this it decreased drastically.

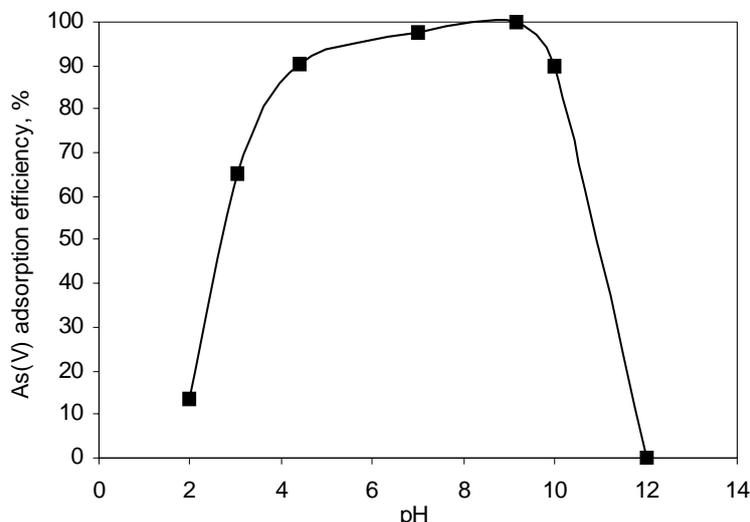


Figure 12. Effect of pH on adsorption of As(V) onto a calcined (350°C) low bulk density BAS powder (Adsorbent quantity- 0.08g, As(V)- 12.2ppm, 0.61 mg)

3.2. Adsorption of arsenic (III)

Adsorption of arsenic (III) was carried out using all the three materials. Adsorption of As(III) onto uncalcined and various calcined powders for both fine gibbsite and low bulk density gel hydroxide (BAS) were shown in Figure 13. It has been found that maximum adsorption was obtained at around 350°C for fine gibbsite powder but below and above this calcinations temperature and for uncalcined powder it decreased. Uncalcined powder showed 5.2% adsorption while that at 350°C (boehmite) 86% and at 1200°C it has dropped to 4.6%. For low bulk density BAS powder at 350°C, only 13% adsorption was found but maximum adsorption of 52% was obtained at 900°C. Above this temperature arsenic (III) adsorption has dropped considerably. For coarse boehmite material maximum adsorption was found to be around 80%. Adsorption kinetics of the materials was carried out with different calcined products.

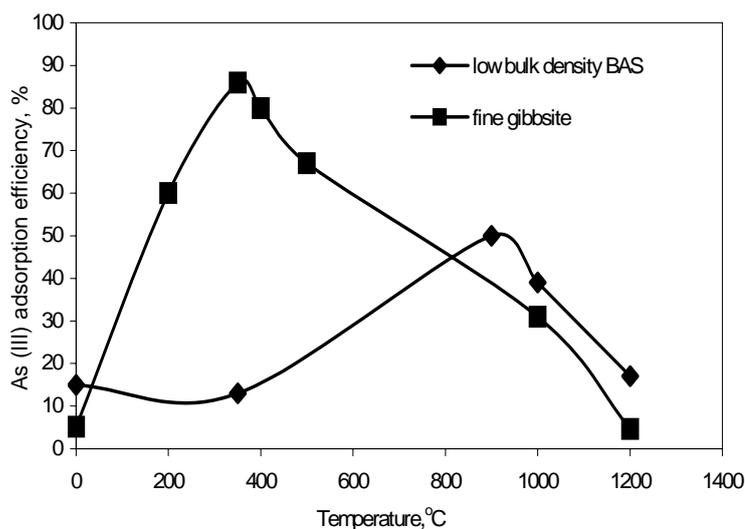


Figure 13. Adsorption of As(III) onto uncalcined and different calcined powders as a function of calcination temperature (Adsorbent -0.5g, As(III)-7.2ppm, 0.36mg)

Figure 14 shows the adsorption of As(III) onto different calcined products as a function of time. Arsenic (III) adsorption onto low bulk density calcined BAS (350°C) particle was found very less (24%) after 180min. of contact time compared to fine boehmite powder. This observation is quite opposite to that of Arsenic (V). In case of As(V), adsorption onto low bulk density powder was higher than fine boehmite. In case of low bulk density BAS, calcined at 900°C (η -alumina) adsorption of As(III) was 52%. It was found that As(III) adsorption occurred mostly on boehmite phase obtained after calcination at 350°C and 400°C for fine and coarse gibbsite particles respectively. It may be possible to adsorb total As(III) by adjusting the heat treatment condition. Higher adsorbability of As(III) onto fine and coarse boehmite compared to that of low bulk density material indicated that As(III) adsorption depend more on surface area. In each cases it was observed that higher the surface area more the As(III) adsorption efficiency. Surface areas of fine and coarse boehmite are much higher than the low bulk density BAS as shown in Figure 2.

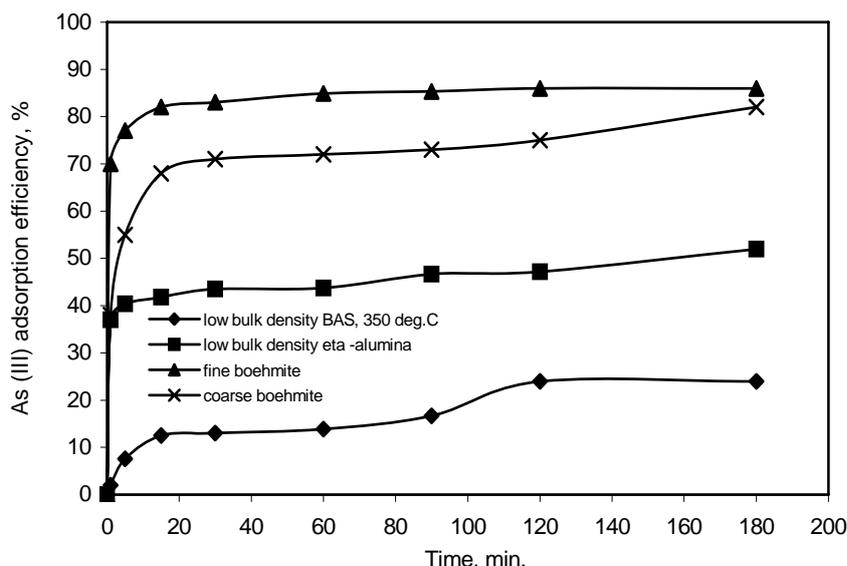


Figure 14. Adsorption of As(III) onto different calcined powders as a function of time (Adsorbent-1.5g, As(III) -7.2ppm, 1.08mg, Temp.-ambient)

In sum, it was found that adsorption of As(V) is more effective onto low bulk density BAS powder. In fact 100% adsorption was noticed with this powder when calcined between 250-350°C and at 900°C. Between 250-350°C substantial amount of dehydroxylation took place but this might not be the reason for 100% adsorption. It has been infact observed minimum of 96-98% adsorption throughout up to 900°C. But beyond 900°C calcination temperature adsorption fell drastically. Uncalcined BAS powder has surface area of around 45m²/g and on heating it decreased. This amorphous material therefore has major lattice imperfections and active sites at the uncalcined condition compare to that of fine gibbsite, which is more ordered in uncalcined condition. This may be the reason that the material has high adsorption capacity all through the calcination temperatures up to 900°C. At 900°C, the η -alumina phase crystallizes, at this condition material had high degree of dehydroxylation and complete desulfurisation. This metastable lattice structure along with desulfurisation might helped in activity enhancement. The BET surface area has become doubled at 900°C. It has been observed that 350°C calcined BAS powder and boehmite had dehydroxylation of 75-78% whereas for η -alumina it was around 97% including desulfurisation while excluding desulfurisation, the dehydroxylation degree was found to be similar as 75 to 78%. Adsorption of As(III) onto calcined and uncalcined low bulk density BAS showed quite opposite trend. Adsorption of As(III) onto this material was found to be very less even with higher quantity of adsorbent. The maximum adsorption obtained for 900°C (η -alumina) material where only 52% adsorption was noticed. 350°C calcined BAS showed only 24% adsorption for As(III) after 180min. contact time whereas for As(V) it was 100%. It, therefore, indicate that active sites responsible for As(V) are different than As(III). The fine boehmite (calcined at 350°C) was found to be more effective than coarse particles. Adsorption of As(III) was found 86% for fine and around 80% for coarse particles. But quantity of adsorbent required was 3 times to that of As(V) case. As(V) adsorption was 92% and 80% for fine and coarse boehmite respectively. Under similar adsorbent quantities. Higher adsorbability was noticed with higher quantities of adsorbent. The reason for high adsorbability for both As(III) and As(V) onto boehmite particles may be explained as follows. Fine and coarse gibbsite on heating at 300-400°C produces boehmite, which is an oxyhydroxide

phase of aluminium. This boehmite structure was obtained after 75-78% dehydroxylation that imparted defect structure in the lattice and optimal concentration of surface hydroxyls. Further the surface area also attained its peak at 350-400°C. The combination of above parameters probably responsible for adsorption of As(III) and As(V). Boehmite obtained from other than gibbsite source or directly precipitated boehmite may not produce similar adsorption activity. Further, by observing adsorbability of all the adsorbents, it was found that As(III) adsorption mostly depends on the surface area rather than combination of surface morphology and surface area. This is because adsorption efficiencies were found to be increasing with increase in BET surface area for materials such as 350°C calcined BAS, η -alumina, coarse boehmite and fine boehmite (Figures 13 and 14). The metastable forms such as χ and κ were not very attractive for arsenic adsorption because they had dehydroxylation degree more than optimum value and surface areas are also low; this observation is not in agreement with other authors (Wefers *et al.*, 1987; Fleming, 1990; Fleming *et al.*, 1990). The α -alumina formed from gibbsite has no adsorption capacity at all because of total dehydroxylation and formation of a stable phase with minimum possible defect structure. But α -alumina formed from BAS showed higher arsenic adsorbability than α -alumina formed from gibbsite. Effect of temperature showed positive influence on adsorption of As(V). With increase in temperature, adsorption increased for both boehmite and calcined (350°C) BAS powders. This shows the process of As(V) adsorption is endothermic and the adsorption process is known as chemisorption (Fleming *et al.*, 1990; Habashi, 1993). But As(III) adsorption was found to be unaffected with increase in temperature for both the materials. The explanation for this behaviour of temperature dependency vis-à-vis adsorbability of As(V) and As(III) is very difficult to visualize under the studied experimental conditions. But an explanation may be that as the arsenic(III) adsorption mainly dependent on surface area, the increase in temperature, therefore, has no influence on adsorbability. In case of As(V) adsorption, as it is dependent on combined effect of surface properties as discussed earlier, the favourable change of any parameter due to change in temperature will enhance the adsorbability. Further, the adsorption capacity showing decreasing trend with adsorbent quantity indicates the material surface to be heterogeneous.

4. CONCLUSIONS

The study conducted on adsorption of As(V) and As(III) onto various calcined products showed very interesting features. Different starting materials such as precipitated fine ATH, coarse ATH and low bulk density gel hydroxide (basic aluminium sulfates, BAS) were taken for the study. Following are the characteristic features as revealed from the study.

1. Boehmite obtained from fine and coarse gibbsite and η -alumina from amorphous low bulk density gel hydroxide were found to have higher adsorbability than other calcined products. Precipitated uncalcined gibbsite has very less adsorbability for As(V) and for As(III) but uncalcined BAS has higher adsorbability for As(V) and poor for As(III).
2. Low bulk density gel hydroxide showed highly efficient arsenic (V) adsorption for both uncalcined and calcined powders (up to 900°C). The material calcined between 250-350°C and at 900°C could adsorb 100% As(V) with lower quantity of adsorbent than used for fine and coarse boehmite material. But As(III) adsorption was not efficient. The η -alumina formed at 900°C showed only moderate adsorption, when added three times that added for As(V).
3. Fine and coarse ATH material, gibbsitic in nature, calcined at 350°C and 400°C respectively showed high adsorption efficiencies for both As(III) and As(V). 92% As(V) was adsorbed by 350°C calcined fine gibbsite powder whereas 80% adsorption was found for coarse gibbsite powder calcined at 400°C. Experiments are carried out under identical conditions. It has been found that in both the cases boehmite (γ -AlOOH) is the predominant phase. Arsenic (III) adsorption was found to be 86% for 350°C calcined fine gibbsite (boehmite) material and around 80% for 400°C calcined coarse boehmite. Higher adsorption efficiencies were obtained with higher quantities of adsorbents. The adsorbent used for As(III) was almost three times that of As(V) case. Therefore, fine boehmite obtained from gibbsite is found better adsorbent than coarse boehmite.
4. Effect of adsorption temperature has positive influence on the adsorption of As(V) for both fine boehmite and low bulk density BAS. But adsorption of As(III) onto these materials was found to be unaffected with increase in temperature.
5. In case of fine boehmite, the arsenic (V) adsorption was found unaffected in the pH range 2 - 9.15 but beyond 9.15 pH adsorption has dropped. At pH 12 no adsorption was found. For low bulk density powder calcined at 350°C, showed lower adsorption efficiency in acidic pH range and in highly alkaline pH range. But intermediate pH (8-9.15) showed high adsorption efficiency. At pH 12 no adsorption was found.
6. It has been found in overall that transition alumina formed such as χ -alumina (500°C, calcinations) and κ -alumina (1000°C calcinations) from gibbsite showed lower adsorption efficiencies for both As(III) and As(V).

7. The α -alumina formed from BAS showed higher arsenic adsorption efficiency than the α -alumina formed from gibbsite.
8. Adsorption capacity (mg/g) calculated in terms of arsenic adsorbed (mg) per g of adsorbent showed decreasing trend with adsorbent quantity indicating material surface to be heterogeneous in nature.
9. 75-78% dehydroxylation obtained for boehmite transformation and around 97% dehydroxylation including desulfurisation for transitional η -alumina transformation were found to be effective for arsenic adsorption.
10. The surface area was found to have major role in adsorption of As(V) and As(III). The As(V) adsorption depended on combined influence of various parameters such as surface area, dehydroxylation or surface hydroxyl ion concentration, desulfurisation, etc. but As(III) adsorption seems mostly depended on surface area.

5. UNCITED REFERENCE

Khoe *et al.*, 1999

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The adsorption of arsenic onto uncalcined and calcined powders was carried out in a glass vessel of 250ml/500ml capacity covered with a lid. The lid had provision for inserting the stirring rod and an opening for sampling. Figure 7. Adsorption of As(V) onto different calcined coarse gibbsite as a function of calcination temperature (Adsorbent Quantity-0.5g, As(V) - 16.05ppm, 1.605mg). 3.1.3. Adsorption of As(V) onto low bulk density gel aluminium hydroxide (BAS) powder. Figure 8 shows the adsorption of As(V) onto precipitated low bulk density BAS powder and its calcined products at various temperatures. Adsorption of arsenic(V) using iron and aluminum based oxides 3. Arsenate adsorption onto Al₂O₃ as a function of pH at (a) different dosages. and (b) As(V) initial concentrations. 62. The existence of arsenic in a specific oxidation state in the hydrosphere depends on various environmental factors such as reduction-oxidation reactions, pH conditions, general hydrochemistry, microbial activity, and other ionic distribution states, but the concentration of arsenic species mainly depends on redox potential and pH (Masscheleyn et al., 1991; Dzombak and Morrel, 1990; Bering et al., 1996). Abstract Yellow dye (YD) adsorption was carried out on some mesoporous materials such as calcined and uncalcined Al-MCM-41. These two matrices were synthesized by variation of Si/Al molar ratio (20, 40 and 80) under thermal conditions. The obtained materials were characterized by various methods: XRD diffraction (XRD), nitrogen adsorption at 77K, Fourier transformed infrared spectroscopy (FTIR) and energy dispersive spectroscopy by X-rays (EDX). Elimination of YD as a function of both pH and shaking, contacting time, and reaction temperature was studied. The uncalcined Al-MCM-41 had the highest