

Efficient Removal of Arsenic from Polluted Ground Water

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Abstract: Arsenic concentration in the polluted ground water has been sufficiently reduced from its alarming limit to a permissible one ($\sim 0.02 \text{ mg L}^{-1}$) employing the intercalation behaviour of Layered Double Hydroxide (LDH) Mg-Al hydrotalcite. The exchange reaction was very simple and the efficiency of the process remained almost same after many cycles. This efficiency of arsenic removal from contaminated ground water has been drastically improved using pre-treatment with a small amount of dilute aqueous H_2O_2 to oxidize As^{3+} to As^{5+} under mild acid pH condition and followed by its exchange with hydrotalcite. After few exchange cycles the solid exchanger could be easily exchanged with a saturated NaCl solution to regenerate the LDH for further use.

Key words: Arsenic, hydrotalcite, ion exchange, pollution, water purification

INTRODUCTION

Arsenic is well known for its deadly human poison for long and its intake in large quantities could cause different skin, metabolic and cardiac disorder leading to death. Both soil and underground water of a widespread area of our world today has been threatened with acute arsenic contamination^[1-3] for last few years, affecting health of the millions of people. Drinking of contaminated ground water causes many deadly diseases^[4-8]. The highest contamination of arsenic in underground (drinking) water observed in those areas are far above the standard set by World Health Organization (WHO) for arsenic between 0.01 and 0.05 mg L^{-1} ^[9]. Most of the technologies available today for the removal of arsenic perform most efficiently when arsenic is available in the form of As^{5+} ^[10,11]. Ground water, however, is mostly contaminated by As^{3+} . As^{3+} could be converted through pre-oxidation to As^{5+} by oxidants like Cl_2 , FeCl_3 , KMnO_4 , O_3 , etc. or dioxygen in the presence of ultraviolet rays^[12]. After these pre-oxidation, Arsenic⁵⁺ species could be removed more efficiently, however, such technologies have not been in use so far. Oxidation/precipitation, coagulation/filtration (C/F), lime softening (LS), adsorption on activated alumina (AA), nanofiltration (NF), electrodialysis (ED), reverse osmosis (RO), ion exchange (IE), etc. are commonly used technologies for the removal of arsenic from water, each of which have their own limitations^[10]. In C/F, coagulant and dosage used could

affect the efficiency of the process. Systems using LS may require secondary treatment to meet that goal. AA is effective in treating water with high total dissolved solids and in this removal process presence of Fe^{3+} in the ground water was found to be helpful to oxidize part of As^{3+} into As^{5+} ^[13]. AA is highly selective towards As^{5+} ; and these strong attraction resulted in regeneration problems, leading to 5-10% loss of adsorptive capacity for each run. Moreover, the water purifiers for arsenic removal available in commercial scale today using these technologies are quite expensive. Although LDH based anion exchangers have been used recently for the removal of arsenic from waste water^[14-17], efficiency of such process was low and little work have been done on the role of different oxidation state of arsenic on such removal processes. It is pertinent to mention that fungus *Hymenoscyphus ericae*, is well known for the extraction of arsenic from soil through hyperaccumulation^[18] and it can reduce the poisoning of underground biomass. High concentration of arsenic in the underground biomass^[19] is mainly responsible for the arsenic contamination of underground tubewell water through geochemical soil leaching. On the other hand arsenic could be derived from reductive dissolution of arsenic-rich iron oxyhydroxides available in the soil. Disposal of the arsenic-contaminated coagulation sludge from the C/F and LS plants is also of a major environmental concern. Here, this study was designed with the objective for efficient removal of arsenic from the polluted ground water using the intercalation behavior of

LDH Mg-Al hydrotalcite through *in situ* oxidation of As^{3+} using small amount of dilute aqueous H_2O_2 under acid pH condition, followed by its exchange with hydrotalcite.

MATERIALS AND METHODS

Synthesis: The Mg-Al-hydrotalcite exchanger was synthesized by known literature procedure^[20] using a mixture of $MgCl_2 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$ and NaOH. Typically a 0.15 mol NaOH in 60 ml double distilled water was added to an aqueous solution containing 0.1 mol $MgCl_2 \cdot 6H_2O$ and 0.033 mol $AlCl_3 \cdot 6H_2O$ in 120 ml of water maintaining a pH at Ca 10.0. During addition gaseous N_2 was bubbled through the suspension to avoid adsorption of CO_2 from ambient air. The hydrothermal treatment of the co-precipitated gel was carried out hydrothermally at 343 K for 1D in a closed polypropylene vessel under constant stirring condition.

Characterization: The as-synthesized hydrotalcite sample was calcined at 500 K in the flow of air for 4 h followed by heating under vacuum at 373 K for 1 h prior to the exchange studies. The as-synthesized as well as template free samples were identified by powder XRD using a Shimadzu XRD-6000 diffractometer with $Cu-K_{\alpha}$ radiation ($\lambda=0.15406$ nm) at 35 kV and 20 mA. BET surface areas were measured from the respective nitrogen adsorption isotherms (between $P/P_0=0-0.3$) using a BELSORP 28SA at 77 K. FT-IR spectrums of different samples were recorded in a Nicolet MAGNA-IR 750 Spectrometer Series II using KBr pallets. Philips XI-30/FEG, XL-serial Scanning Electron Microscopy with an EDS (New XL-30) attachment was used for the determination of morphology and surface chemical composition. Flow injection hydride generation attachment in atomic absorption spectrophotometer (Perkin Elmer AAS 3310) has been used for the detection of arsenic in these water samples before and after exchange reaction. The detection limit of F1-Hg-AAS was 3 ppb with 95% accuracy.

Ion-exchange: Various standard arsenic containing solutions as well as ground water collected from different arsenic affected areas were studied. Typical representative ground water samples collected from a two arsenic-affected areas of West Bengal, India, samples A and B and their exchange data are shown in Table 1. In a typical experiment, 100 g of the polluted ground water containing arsenic was stirred with 1 g of the preheated hydrotalcite at 298 K for 1 h with an O_2 atmosphere maintained inside the closed reaction vessel. For the pre-oxidation step small amount of dilute aqueous

hydrogen peroxide (30%) and concentrated HCl were added to the sample water to convert the As^{3+} to As^{5+} initially. Then the resultant aqueous solution was exchanged with the hydrotalcite similarly at 298 K for 1 h. After the ion exchange the content was filtered. Arsenic content of the ground water before and after the exchange was estimated by atomic absorption spectroscopy.

RESULTS AND DISCUSSION

Characterization of LDH: XRD patterns of the hydrotalcite sample (a, as-synthesized hydrotalcite with Mg/Al=3 in the gel, 2.9 in the product) at different stages illustrated in Fig. 1. The peak positions and their intensity ratios matched well with those of the standard data^[21,22]. After calcination at 500 K peak pattern remained same, however, these peak positions were shifted towards lower 2θ (higher interlayer spacing, 7.92 Å) with little change in the intensities (Fig. 1b). After $As^{3+/5+}$ exchange from water interlayer spacing further increased to 8.03 Å with the appearance of an additional peak at $d=3.65$ Å. Little change in lattice spacing (d_{003}) could be attributed to the interlayer anion exchange. Changes in interlayer spacing agree well with the expected d spacing^[21,22] from the size of the exchanging anion, their partial substitution and corresponding charge. This peak disappeared after re-activation by exchanging the As-containing solid with aqueous NaCl solution. Presence of this type of additional

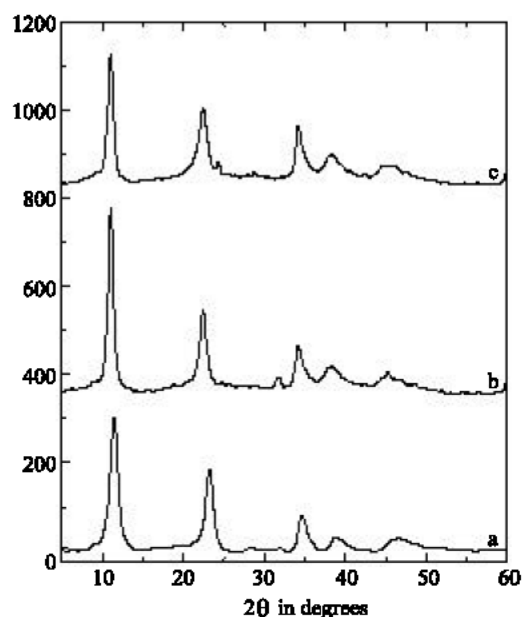


Fig. 1: X-Ray diffraction pattern of as-synthesized Mg-Al-Cl hydrotalcite (a), same after calcination at 500 K (b) and after $As^{3/5+}$ exchange ©

Table 1: Exchange data of various arsenic containing solutions over hydrotalcite¹

Entry	Solution type ²	Arsenic content (mg L ⁻¹)		Arsenic removal efficiency, %
		Before	After	
1.	0.09629 g NaAsO ₂ +100 g double distilled H ₂ O (10.7-9.8)	555.000	142.000	74.4
2.	0.09866 g NaAsO ₂ +100 g double distilled H ₂ O+0.2 g H ₂ O ₂ +0.1 g HCl (5.28-7.14)	569.000	48.000	91.7
3.	0.09947 g NaAsO ₂ rest same as entry 2 after three exchange cycle (5.17-7.02).	577.000	59.000	89.8
4.	100 g sample A H ₂ O (8.9-9.4)	0.135	0.067	50.4
5.	100 g sample A H ₂ O+0.22 g H ₂ O ₂ +0.10 g HCl (4.8-6.2)	0.135	0.021	84.4
6.	100 g sample A H ₂ O rest same as entry 5, exchanger after three exchange cycle (4.65-6.1)	0.135	0.023	82.9
7.	100 g sample B H ₂ O (8.72-9.55)	0.109	0.058	46.8
8.	100 g sample B H ₂ O+0.22 g H ₂ O ₂ +0.10 g HCl (5.12-6.7)	0.109	0.016	85.3

¹Solution for each entry was treated with 1.0 g pre-treated Mg-Al hydrotalcite for 1 h at 298 K in a closed reaction vessel under O₂ atmosphere. Double distilled water with As below AAS detectable limit was used for the preparation of the standard As³⁺/As⁵⁺ solutions

²Values in parenthesis shows pH value at 0 and 1 h of exchange

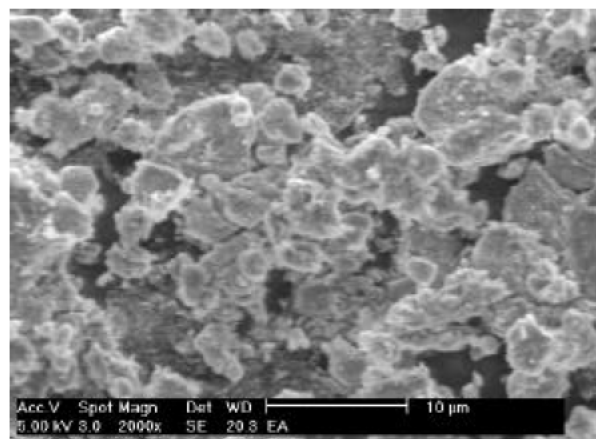


Fig. 2: SEM image of the LDH exchanger

peak have been explained by Vucelic *et al.*^[23] due to location of benzoate anions in a superlattice of the ab-plane of hydrotalcite. Thus these results suggested that the AsO₄³⁻ was located in between brucite layers through an anion exchange.

BET surface areas of as-synthesized sample dried at 373 K, 500 K and after first exchange with water sample A were measured from the respective N₂ adsorption isotherms and they were 108, 87 and 81 m²g⁻¹, respectively. In the FT IR spectra of the pre-heated LDH sample at 500 K, a strong and broad peak in the region 3500-3665 cm⁻¹ was observed. This could be ascribed due to structural OH⁻ groups, valence vibrations of OH...OH and/or M-OH in the Mg-Al-hydrotalcite. Other peaks at 3465 cm⁻¹ could be attributable to Al-OH stretching and 1651 cm⁻¹ due to interlayer water was also observed as previously assigned^[24]. In Fig. 2 the SEM image of the Mg-Al-LDH sample is shown. Small plate like crystallites of 1-3 µm size was observed. EDS analysis also revealed homogeneous distribution of Mg and Al (Mg/Al ratio in different positions varied from 2.80-2.92) atoms in the crystallites.

Exchange reaction: The exchange studies of various arsenic contaminated solutions were shown in Table 1. In all the cases total arsenic content in the water reduced considerably after the exchange of the arsenic containing solutions with the hydrotalcite exchanger. As shown in Table 1 (entry 1, 4 and 7 vis-à-vis 2, 5 and 8, respectively) the efficiencies for arsenic removal increased drastically using pre-oxidation step before the ion-exchange process indicating that the exchange efficiency of As⁵⁺ species for the interlayer anions are higher compared to that of As³⁺. Standard sodium arsenite solutions were made in arsenic-free water and these were used for entries 1-3. Identical exchange studies were repeated four times for each sample of water and as well as that of sodium arsenite solution made in double distilled water (arsenic content below the detectable limit of AAS) and in all the cases high efficiency for arsenic removal were observed (viz. entries 3 and 6).

Most common valence states of arsenic observed in water are arsenate As⁵⁺, which occurred mostly in aerobic surface waters. Whereas, As³⁺ arsenite, could be observed in anaerobic ground waters^[25]. In the pH range of 4 to 8, the predominant As⁵⁺ species are H₂AsO₄⁻ and HAsO₄²⁻, negatively charged and thus more suitable to get exchanged by an anion exchanger whereas, As³⁺ mostly remained as nonionized H₃AsO₃. Both As³⁺ and As⁵⁺ species are significantly present in the contaminated groundwater; As³⁺ constitutes about 25-50% of the total dissolved arsenic. Mg-Al-Cl hydrotalcites are brucite-like layered double hydroxide (LDH) with Cl⁻ anions and water molecules are located in between the positively charged metal hydroxide layer and are well known to be freely intercalated by similar type of anions^[26,27]. When this contaminated water was allowed to exchange with Mg-Al-Cl LDH, the interlayer anions get exchanged with H₂AsO₄⁻ and HAsO₄²⁻ and thus the resulting water becomes free from arsenic contamination. Nonionized As³⁺ could be easily converted to H₂AsO₄⁻ and HAsO₄²⁻ under mild oxidation with dilute H₂O₂ under acidic pH.

Thus this contaminated water could be more efficiently get exchanged for the interlayer anions due to high negative charge density. Very small amount of dilute aqueous H_2O_2 and HCl in the pre-oxidation step was used. H_2O_2 /HCl system being chosen to oxidize As^{3+} because of its high reduction potential and H_2O and Cl^- being the clean byproducts. pH change during addition and exchange process were given in Table 1. For example in entry 2, initial pH of water was 6.8, after the addition of $NaAsO_2$ it became 10.7, then after the addition of H_2O_2 /HCl pH became 1.92, 0 h after the addition of Mg-Al-Cl pH was 5.28 and then after 6 h ion exchange pH was 7.14. An increase in the solution pH occurred gradually as the exchange goes to completion. This could be ascribed due to the exchange of OH^- present partially in the hydrotalcite materials with arsenic species in the solution. Moreover, the $H_2AsO_4^-$ and $HAsO_4^{2-}$ anions present in the contaminated water being replaced by interlayer anions, helped to enhance the pH during ion-exchange.

Regeneration of the exchanger: After three exchange-cycles being repeated with the same solid Mg-Al-hydrotalcite, the exchanger was treated with 100 ml 0.5 N NaCl solution for 6 h at 298 K and filtered. Arsenic was not detected in the solid (by EDS) after NaCl exchange and the basal spacing again reduced to 7.90 Å. These data suggested that the intercalation process was reversible in nature.

Recycling of the exchanger: Mg-Al-hydrotalcite could be easily separated from the reaction mixture by simple filtration after the exchange reaction. The recovered hydrotalcite have been used twice for the next oxidation (Table 1), although a slight decrease of the exchange efficiency was observed in the third run using hydrotalcite as exchanger for As^{3+}/As^{5+} containing solution (Table 1).

LDH based anionic exchanger, inexpensive and easy to use, could be used for the efficient removal of arsenic from polluted ground water. Pre-oxidation of nonionic As^{3+} to negatively charged As^{5+} species using dilute hydrogen peroxide as oxidant has been found to have a dramatic effect in enhancing the arsenic removal efficiency. This result indicated the high charge density of the anion speeded up the exchange process. Exchange efficiency of the hydrotalcite was very good and it could be regenerated with aqueous NaCl solution without any appreciable loss of activity after few exchange runs.

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