ADSORPTION OF ARSENIC COMPONENTS ON LAYERED DOUBLE HYDROXIDES AND MIXED OXIDES FOR WATER PURIFICATION

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Abstract
Aim of this research was the removal of toxic and carcinogenic arsenate (AsO_4^{3-}) ions from drinking water with different metals (Mg, Mn, Al, Fe) content layered double hydroxides (LDH). The efficiency of the MgAl LDHs in the arsenic removal is increased with increasing nitrate content in LDH. The basal spacing of LDH was decreasing with 0.085 nm after ion-exchange. The calcinated form of each adsorbent resulted less arsenic removal, but less dissolution of metal from the oxide compared to the uncalcinated LDH. Increasing the manganese content in the MnFe LDH resulted in enhanced arsenic removal efficiency.

Keywords:
arsenic removal, drinking water, layered double hydroxide, adsorption, calcination

1. INTRODUCTION

Arsenic is a human genotoxin and chronic exposure is associated with development of cancers, including skin cancer [1]. The inorganic arsenic forms are metabolically inhibitors. Arsenate (As^{5+}) displaces the phosphate ion from the energy source ATP molecule, arsenite (As^{3+}) bonds with sulfhydril group of the proteins (e.g. glutathione) and it inhibit their function. By United States Environmental Protection Agency (USEPA) 0.3 g/kg/day sanitary threshold of arsenic was accepted on the basic of statistics data. The Europen and World Health Organization (WHO) limit of arsenic content of drinking warter is 10 g/L. The arsenic accumulate in some groundwater and mineral by natural process [2, 3, 4, 5]. The arsenic atom displaces silicium, iron and aluminium atoms in the crystal latice and this fact causes the high arsenic content of minerals. In the Pannonian basin the arsenic accumulate in the Pleistocene sediments by the rivers and the subsurface flows [6]. This arsenic content resolving into the groundwater from the 100-300 m deep strata. In our days the arsenic contamination in the groundwater is serious problem all over the world [7, 8]. An estimated 57 million people may be drinking high arsenic content water in Bangladesh and West Bengal, India. The strong antropogenic effect (e.g. mining, agriculture) is increasing the arsenic content of surface water, groundwater and soil [9]. The pH of groundwaters is between 6.5-9.5, the non-dissociated (H_3AsO_3) and monovalent anionic ($H_2AsO_3^-$) natural forms of arsenite are and arsenate exits in anionic forms ($H_2AsO_4^{1-}$, $HAsO_4^{2-}$) in this mildly alkaline range [10]. The arsenic forms and the geochemical components of groundwater determinate the applicable water treatment technology. In Hungary the removal of arsenic from drinking water with iron (III)-hydroxide is one of the current methods. The average efficiency is 60-80 % that can increase up to 95 % with optimized parameters. Granulated iron hydroxide (GEH) column is applied in numerous water plants. Goethite (FeOOH) and iron hydroxide are the component of GEH column. Arsenic removal efficiency of natural or synthetic iron oxides and hydroxides are examined in number of publications [11, 12, 13, 14]. T. Tuutijärvi et al. investigated the arsenate adsorption capacity of different size maghemite nanoparticles in a wide pH range [15]. Large advantage of these superparamagnetic is that the nanoparticles can be easily removed with magnetic field from treated water. Zero-valent iron particle removes arsenate and arsenite with high efficiency in natural groundwaters by adsorption, surface precipitation, and co-precipitation with various corrosion products [16, 17, 18]. Membrane processes (nanofiltration) are suited for arsenate release, but are not efficient by the arsenite content groundwaters [19, 20]. The arsenic removal is enhanced by

the hybrid membrane treatments [21, 22]. The layered double hydroxides (LDH) are one group of layered structured minerals in the nature. The sheets of the layered double hydroxide are formed from divalent metal ions (M^{2+}: Mg^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}) and trivalent metals ions (M^{3+}: Al^{3+}, Fe^{3+}) and exchangeable anions (A^{n-}: CO_3^{2-}, SO_4^{2-}, NO_3^{-}, Cl^{-}) compensate the positive surface charge between the layers ($[M_{1-x}^{2+}M_x^{3+}(OH)_2]A^{n-}{}_{x/n} \cdot yH_2O$). LDHs are applied as adsorber [23], catalyst [24], support in medicine [25], thin film component [26]. The positively surface charged LDH is suited for adsorb the negatively charged arsenic ion forms [27, 28, 29].

2. MATERIALS

Magnesium nitrate hexahydrate ($Mg(NO_3)_2$ $6H_2O$, puriss., Fluka), aluminium nitrate nonahydrate ($Al(NO_3)_3$ $9H_2O$, puriss.), iron (III) chloride hexahidrate ($FeCl_3$ $6H_2O$, analytical grade, Reanal Hungary), manganese sulphate hydrate ($Mn(SO_4)$ H_2O, analytical grade), sodium hydroxide (NaOH, analytical grade), and sodium nitrate ($NaNO_3$, puriss.) were used to prepare layered double hydroxide. Potassium iodide (KI, puriss.), ascorbic acid ($C_6H_8O_6$ analytical grade), pyridine (C_5H_5N, analytical grade), potassium carbonate (K_2CO_3, puriss., MOLAR Hungary), and sodium borohydride ($NaBH_4$, purum), silver diethyldithiocarbamate, Ag-DDTC ($C_5H_{10}AgNS_2$, puriss., Fluka) were used for arsenic(V) determination. Arsenic removal measurements employed the natur arsenic content groundwater and aqueous solution of disodium hydrogenarsenate heptahydrate ($AsHNa_2O_4$ $7H_2O$, puriss., Fluka). The model groundwater originates from Gyula, town of Békés Country, in Hungary (Table 1).

Table 1 The chemical analysis of groundwater from Gyula

	Groundwater analysis	
	07. 2005.	05. 2006.
pH	8.33	8.69
General hardness,°dH	2.0	-
General hardness[a]	-	17.0 CaO
Conductivity, μS	681	528
Sodium[a]	100	-
Potassium[a]	1.0	-
Calcium[a]	10.0	9.2
Magnesium[a]	2.0	1.6
Chloride[a]	27.7	-
Hydrocarbonate[a]	360	-
Sulfate[a]	7.7	-
Arsenic[a]	**0.105**	**0.100**
Ammonium[a]	-	0.60
Nitrite[a]	-	<0.01
Nitrate[a]	-	<0.07
Iron (II)[a]	-	0.043
Manganese (II)[a]	-	0.010
Boron[a]	-	0.38
Total Phosphor[a]	-	0.56
Alkalinity[a]	-	6.4
Dry matter[a]	396.6	-
COI	5.6	3.6

[a] concentration in mg/L

3. METHODS

Arsenic content was determined by silver diethyldithiocarbamate (Ag-DDTC) spectrophotometric methods. Reduction of As(V) by potassium iodide produced arsenic hydride (AsH_3), which was transferred to the pyridine solution of Ag-DDTC by the generated carbon dioxide. The reaction of AsH_3 and Ag-DDTC led to the formation of a colourful compound, whose absorbance was determined in an UVICON UV-VIS spectrophotometer (λ_{max}=540 nm). XRD experiments were carried out in a Philips X-ray diffractometer (PW 1930 generator, PW 1820 goniometer) with CuK-α radiation (λ = 0.15418 nm), 40 kV, 35 mA. Basal spacing was calculated from the reflection angle using the Bragg equation. The amounts of Mg^{2+} and Al^{3+} ions constituting the octahedral layers of double hydroxides were determined in a Jobin Yvon 24 sequential Inductively Coupled Plasma-Atomic Emission spectrometer. For nitrate anion determination, nitrate (NO_3^{-}) ions were converted to yellow nitrobenzene to be determined by photometry [30]. Carbonate (CO_3^{2-}) anions were determined by volumetric in the form of carbon dioxide. The amount of carbon dioxide was calculated by the gas law from the volume of the gas generated within the closed system [31].

Synthesis of layered double hydroxides and oxides

The salt of divalent ion (Mg^{2+} or Mn^{2+}) and trivalent ion (Al^{3+} or Fe^{3+}) were dissolved in 30 mL water at a M^{2+}:M^{3+} molar ratio of 2:1. The MnFe LDH was synthesized at 1:1 and 0.5:1 molar ratios. 25 g of sodium hydroxide and 20 g of sodium nitrate were also dissolved in 170 mL water. Under vigorous stirring, alkaline solution was added dropwise to divalent and trivalent ion content solution in 3 min. The slurry was stirred at 25 ºC for 20 minutes. The sediment was centrifuged, washed once with distilled water and centrifuged again; the product was then dried at 65 ºC. The pH of the MgAl-LDH dispersion was adjusted to 9.1, 9.6 and 13.1 using 0.1 M NaOH and 0.1 M HNO_3. One portion of LDHs was calcinated in air atmosphere at 500 ºC during 10 hours.

Arsenic removal experiments in column

We used both open ended glass tube (250 mm long and 22 mm diameter). The similar amount of adsorbent was top of the filter bad (fibreglass, 5.0 g ion-free sand, 5.0 g quartz with 270 mm

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diameter). The treated groundwater circulated with 33-42 mL /min flow speed by peristaltic pump. 4.0 litre of groundwater was in the closed system and the residual arsenic concentration was determined every third hours. The treated groundwater was exchanged to fresh water then the arsenic concentration achieved the limit. The measured arsenic concentration stop indicated that the arsenic removal column saturated.

4. RESULTS AND DISCUSSION

In many places from Hungary arsenic content exceeds the health limit in drinking water. The arsenic content of water produced in commercially available sodas is illustrated in Figure 1. In more than half of sodas from the Dél-Alföld arsenic content are above 10 µg/L, and in one of the samples is 10 times of the limit. In Hungary all settlements should be 10 µg/L of the arsenic content in drinking water till 2009.
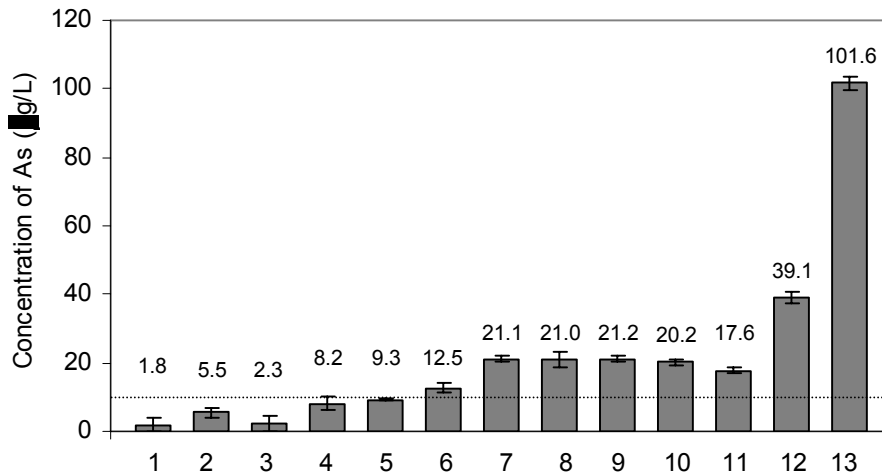

Figure 1. Arsenic content of different commercial sodas from Hungary

In each of a series of 100 ml aliquots of arsenic content solution and 0.01-0.1 g of the adsorbent was suspended; after 5 min of intensive stirring, the adsorbent was removed by filtration. The equilibrium concentration of arsenic in the filtrate was determined. The specific excess adsorption of arsenic ($n^{\sigma (v)}$) was calculated by the (1) equation where V is the total amount of water, c_o and c_e are the initial and equilibrium concentrations, of arsenic respectively, and m is the mass of the adsorbent.
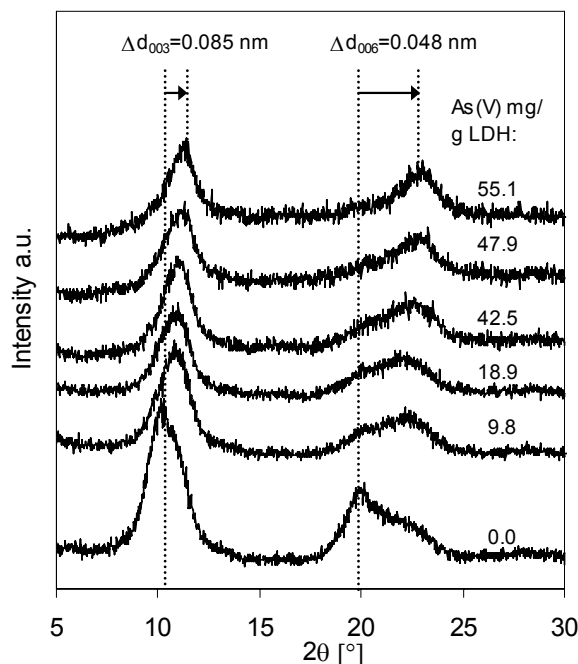
$$n^{\sigma (v)} = V (c_o - c_e)/m \qquad (1)$$

The 2:1 MgAl-LDH was investigated at 0.1 and 150 mg/ L arsenic initial concentration in distilled water. The As(V)-containing dispersed LDH particles were dried at room temperature after adsorption and studied by X-ray diffraction in an air-dry state (Fig. 2). When the amount of adsorbed As(V) increased, the basal spacing gradually decreases with 0.085 nm and this clearly indicates the ion exchange taking place between the LDH layers. The reason for the decrease in basal spacing with increasing arsenate content is that an increasing number of nitrate anions are exchanged in the interlamellar space and the incorporating As(V) species also displace water molecules.

Different amount of 60 °C dried MgAl-, MnAl-, and MnFe-LDHs and the calcined adsorbents were added to the groundwater from Gyula. The groundwater was left in air atmosphere five days before the arsenic removal experiments in order to oxidise the total arsenite content to arsenate form. In case of the 2:1 MgAl-LDH at pH 13.1 the sample obtained nitrate/ carbonate ratio of 0.1, while the pH was 9.6 or

Figure 2. XRD pattern of adsorbed arsenic containing 2:1 MgAl-LDH

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9.1, these values show 0.8 or 1.8. The molar ratio of Mg and Al ions constituting the octahedral layers was nearly 2:1 in the samples and could not influence the ion exchange of arsenate. The MgAl molar ratios are 1.91, 2.06 and 2.13 with increasing nitrate/carbonate molar ratio. Effect of nitrate/carbonate molar ratio between the layers was investigated by the 2:1 MgAl-LDH. The arsenic removal efficiency in percentage calculated by the (2) equation where c_o and c_e are the initial and equilibrium arsenic concentrations.

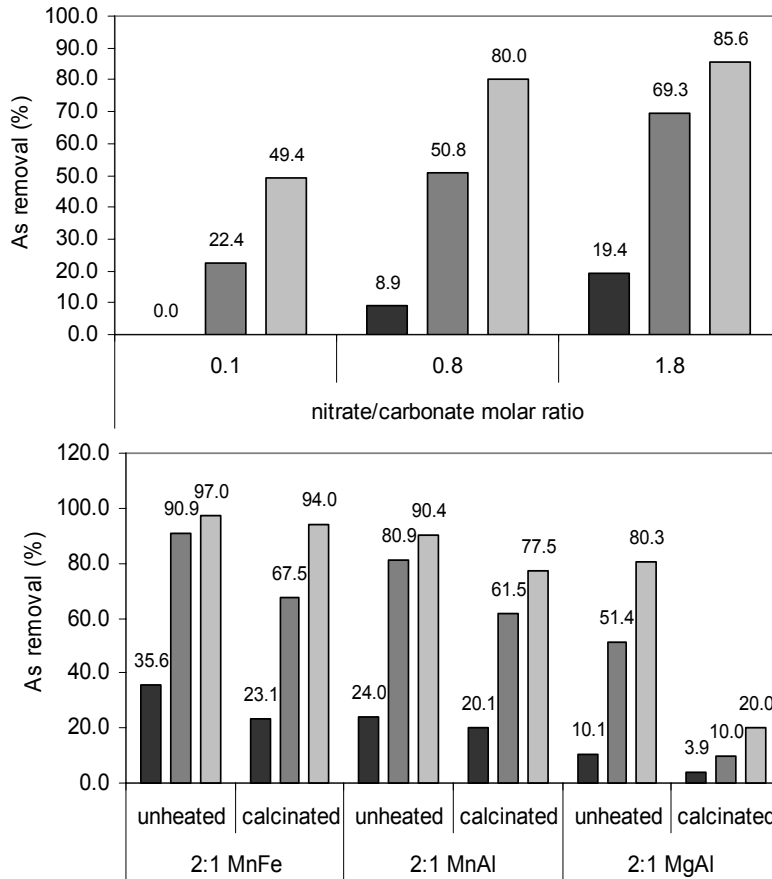$$As\ removal\ (\%) = [(c_o-c_e)/c_o]\ 100 \tag{2}$$

Figure 3. Arsenic removal efficiency of 2:1 MgAl-LDHs at different nitrate/carbonate molar ratio in the groundwater (0.1 ■, 0.5 ■, 1.0 ■, g LDH /L)

The arsenic adsorption capacity is increasing with increasing nitrate content of LDH (Fig. 3). At the lowest 0.1 NO_3^-/CO_3^{2-} ratio the adsorption capacity is less than 1.8 ionic ratio, because carbonate may be irreversibly bound. The explanation is that greater atmospheric carbon dioxide is dissolved during the synthesis of LDH at higher pH. When the type of metal ions at 2:1 molar ratio LDH sheets were changed than different specific arsenic removal efficiencies were obtained in the treated water (Fig. 4).

Figure 4. Arsenic removal efficiency of several type of 2:1 LDHs and oxides in the groundwater (0.1 ■, 0.5 ■, 1.0 ■, g LDH /L)

The results show that the 2:1 composition MnAl-LDH is adsorbed 1.5 times more arsenic amount, than the MgAl-LDH at 0.5 g/L adsorbent concentration. The manganese content LDH was bound twice as much arsenate than the magnesium content LDH at larger amount of adsorbent (0.5 and 1.0 g/L). The most successful MnFe-LDH reduced the arsenic content below the limit value in the treated water with 0.5 g/L amount of adsorbent. Calcinations of the various metal ion containing LDHs decreased the efficiency of arsenic removal with less degree than the unheated adsorbent, on contrary to the literature [32, 33]. The adsorbed arsenic content decreases to one fourth through calcination at 1.0 g/L MgAl content adsorbent. This difference decreases between the unheated and calcinated forms of MnAl and MnFe adsorbents. In case of 1.0 g/L of MnFe oxide 13 times more arsenic amount was removed from groundwater compared to that of MgAl oxide. One of the aims was the lower industrial cost; therefore LDHs were synthesized not only in distilled water, but in drinking water. The 2:1 MnAl-LDH adsorbent produced in drinking water removed the less on average 25% of arsenic from the treated water than in distilled water produced form (Fig. 5). In the drinking water synthesized sample can contain other components (e.g. calcium, magnesium) from the drinking water so has less efficiency than the distilled water prepared LDHs. The most arsenate adsorbing MnFe-LDH was investigated in the groundwater, henceforward. The molar ratios of manganese and iron ions were 0.5 and 1.0 during the preparations of LDHs. The different manganese containing dried powder sample was dosed to the fresh groundwater (> 1 day) and the 5 days old groundwater. The Figure 6. and 7. show that the arsenic content was reduced in the treated water by increasing the manganese content in the calcinated adsorbent. The MnFe-LDHs adsorbed less arsenic species in the fresh groundwater through both the arsenite (As3+) arsenate (As5+) content. The arsenite can be removed more efficiently with MnFe oxides than the arsenate. It is noted that the calcinated samples remove less arsenate than the LDHs. There is not such a clear relationship between manganese content of adsorbent and arsenic removal efficiency of the unheated samples. Redissolution of manganese was calculated by the (3) equation where c is the manganese

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concentrations in the groundwater after the treatment and c_{max} is the maximum manganese concentration of samples.

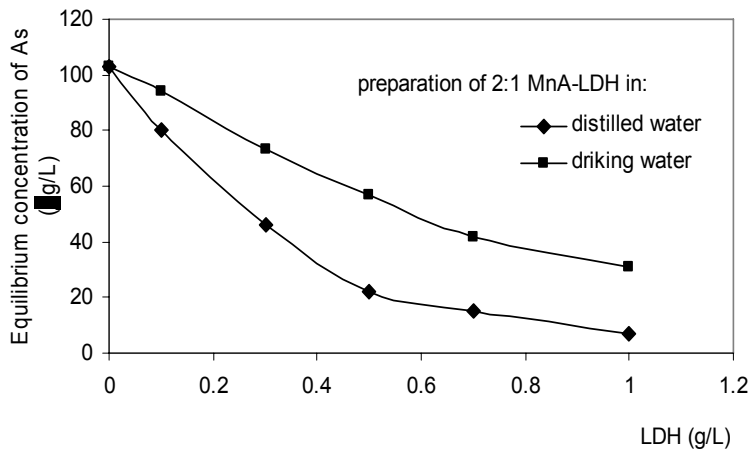$$Mn \text{ redissolution } (\%) = (c / c_{max}) \, 100 \qquad (3)$$

Figure 5. Arsenic conc. in the groundwater after arsenic removal of 2:1 MnAl-LDHs

Redissolution of manganese from the unheated LDHs was increased in proportion to the increase of the solid at the same manganese-iron ratio (Fig. 8). The molar ratio of the manganese-iron was resulted in a greater degree of redissolution of manganese in the treated water at a given amount of investigated adsorbent. Manganese migration is negligible in the arsenic content calcined samples. Therefore, the health-damage of manganese migration could be abolished by the calcination.
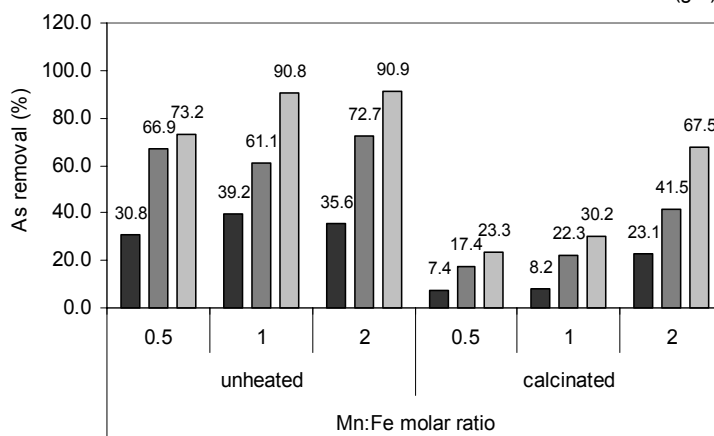
Figure 6. Arsenic removal efficiency of several molar ratio of MnFe LDHs and oxides in the groundwater (0.10 ■, 0.25 ■, 0.50 ■, g LDH /L)

The 2:1 MnFe-LDH precipitated onto the surface of different solid bearer. We investigated the effect of seven different bearers on the arsenic removal of LDH. The MnFe-LDH content bearers were loaded in the glass column. The groundwater was circulated, thus the measured arsenic concentration of the treated water increased below the health limit. In the similar LDH content bearer the GEH adsorbed the most amount arsenate (207 mg/g) and half of this amount was adsorbed by FILTER 4 and BIRM 15 bearer (Fig. 9).
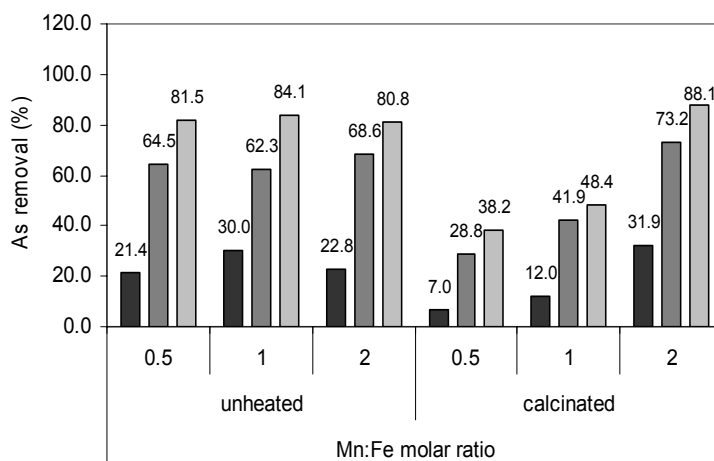
Figure 7. Arsenic removal efficiency of several molar ratio of MnFe LDHs and oxides in the fresh groundwater (0.10 ■, 0.25 ■, 0.50 ■, g LDH /L)

The MTM 15 bearer adsorbed 61 mg arsenic/g from the groundwater. The PIROL 11 and FERMA 16 are the least arsenic removal columns. The GEH without LDH adsorbed 94 mg/g and 41.3 w/w% LDH 69 mg arsenic/g, respectively (Fig. 10). Larger amount of surface LDH inhibited the efficiency, because the LDH particles entirely cover the surface of larger size GEH particles and fill the pores of the bearer. The arsenic removal of indifferent sand bearer was also investigated. The adsorption of arsenate enhanced with increasing MnFe-LDH on the indifferent sand bearer. The 0.8 w/w% LDH content sand bearer column was regenerated with 100 mL of 5 mol/L concentration calcium chloride solution. The 0.2 w/w% of adsorbed arsenic content left for the column after six hours circulation. The arsenic saturated FERMA bearer was tried to regenerate with 1 mol/L concentration sodium chloride solution. The removal of arsenic from the column didn't exceed the 1.0 w/w% in this case. The 6.5 w/w% LDH content GEH was regenerated by 1.0 L of 1.0 mol/L sodium hydroxide. Half of arsenic content of column can be removed after one hour of treatment and further 5-10 % in the next hour.
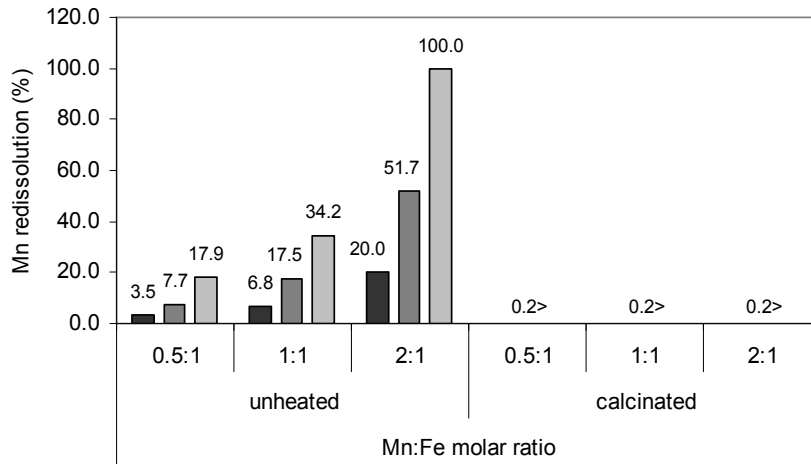
Figure 8. Redissolution of manganese from several molar ratio of MnFe LDHs and oxides after arsenic removal (0.10 ■, 0.25 ■, 0.50 ■, g LDH /L)

Figure 9. Arsenic adsorption capacity of several bearers at similar 2:1 MnFe-LDH content

5. CONCLUSION

Our aims were efficient arsenate removal and production of a cheap adsorbent for industrial application as the syntheses of LDHs were carried out in air atmosphere. When the LDH is synthesized at low pH (pH ~9) value in air atmosphere that little carbonate content and better arsenic adsorber the product will be. The MnFe-LDH at different metal content LDHs adsorbs the most arsenate from the groundwater at same metal molar ratio in the layers.
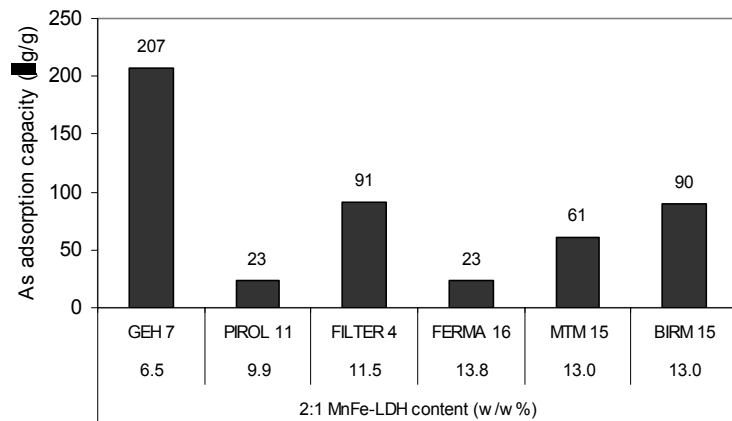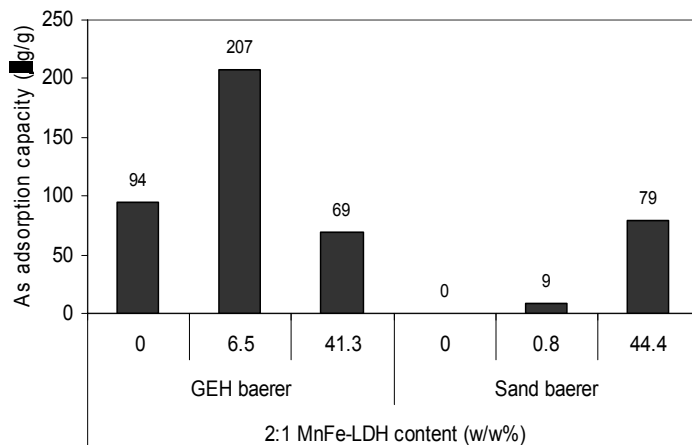

Figure 10. Arsenic adsorption capacity of GEH and sand bearers at different 2:1 MnFe-LDH content

The calcination of MnFe-LDHs decreases the arsenate removal but the binding of arsenite enhance and it dissolves the resolution of manganese from the solid phase. The type of bearer influences the arsenic removal at the column experiments. The best arsenate adsorbent GEH has optimal LDH content by the arsenic release. Sodium hydroxide can be used to regenerate of the LDH content columns.

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