

NEW INORGANIC (AN)ION EXCHANGERS BASED ON (ALKOXIDE-FREE) SOL-GEL GENERATED LAYERED MG-AL HYDROUS OXIDES FOR TARGET ANIONS (ARSENATE, ARSENITE, FLUORIDE, BROMIDE, BROMATE, SELENATE) REMOVAL

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ABSTRACT

In water treatment, adsorption & ion exchange are usually used on the stage of deep purification when higher selectivity to toxic molecules and ions is needed. Inorganic ion exchangers are that class of the adsorptive materials which, if developed by the advanced synthesis approaches, are capable to lower the concentrations of target anions up to the level requesting by World Health Organization (WHO). This paper shows: (1) the new non-traditional sol-gel synthesis of double layered hydrous oxides of Mg-Al comparing them to the previously developed layered Zn-Al and bulk Fe-Al oxides, (2) structure characterization of the Mg-Al hydrous oxides by XRD, N₂ adsorption, SEM, FTIR, and assessment of their surface chemical properties by XPA and potentiometric titration, (3) adsorption isotherms and kinetics of H₂AsO₄⁻ uptake by the new Mg-Al hydrous oxides and adsorptive removal of the other toxic anions: F⁻, Br⁻, BrO₃⁻, HSeO₄⁻, As(III), as well as, (4) mechanism of H₂AsO₄⁻ by FTIR, EXAFS and XPS.

Keywords: Inorganic ion exchange adsorbents, (alk-oxide free) sol-gel, double hydrous oxides, arsenate, arsenite, fluoride, bromide, bromate, selenate

1. INTRODUCTION

WHO announced that, at least, 24% of global diseases are caused by environmental exposure. Water is the most valuable resource of human society and the main factor which defines the level of human brain abilities. Contamination of drinking water with toxic anions is one of the most dangerous contributors which reduce the quality of water. The information about the newly discovered sites contaminated with toxic anions appear in the news every day, what results in the acceleration of deeper toxicological investigations and, then, to the next lowering of maximum permissible levels of the toxic ions. For instance, drinking water standard to arsenic, lowered 5 times in 2004 (from 50 to 10 µg/L), is not considered safe anymore. Recent decision of New Jersey State was to lower it again up to 5 µg/L. Advancement of drinking water treatment technology and replacement of chlorination by ozonation at the disinfection step caused a dangerous side effect: cancerogenic bromate is being formed from bromide originally present in purifying raw waters. In 2004 the next lowering of bromate maximum permissible level dropped this toxicant content down to 10 µg/L, what is not considered as totally safe yet. Removal of any of these anions (Br⁻ or BrO₃⁻

) on the stage (relatively) before or after ozonation is urgent water treatment technology problem which can be solved, first of all, by application of highly selective inorganic ion exchangers. The latest lowering of selenium permissible concentration in drinking water resulted in a new standard of 10 µg/L. In order to reach increasingly stronger drinking water standards, new materials and advanced environmentally friendly and cost-effective technologies, capable to reduce the contaminant concentrations to the required levels are need to be developed.

Ion exchange and adsorption with or without regeneration of the exchanger is a priority purification technique to solve many problems of drinking water treatment including the task of lowering of the target anions (H_2AsO_4 , F^- , Br^- , BrO_3^- , HSeO_4^- et al) concentrations. The list of the materials tested for arsenic and the other anions removal includes carbons (original and pre-treated), zeolites (original and pre-treated), different biomasses and industrial and agricultural byproducts, however, inorganic ion exchanger based on hydrous oxides of Fe, Al, Mn, Mg and the other metals have proved to be the most effective adsorptive materials to solve these water purification tasks. Research investigations for more effective materials, compared to the initially applied activated alumina, led to the recently developed granular ferric hydroxide (GFH), granular ferric oxide (GFO), granular titanium dioxide (TiO_2), and modified activated alumina (MAA).

Earlier researches [1-2] showed highly competitive sol-gel generated Zn-Al hydrous oxides with arsenate removal capacity up to 120 mg[As] $\text{g}_{\text{dw}}^{-1}$. The next task was to develop another double hydrous oxide which would contain magnesium (Mg) in the composition instead of zinc (Zn). The task was achieved and shown in this paper.

2. RESULTS

2.1 Synthesis

Advantageous of sol-gel synthesis, which produces strong and homogeneous materials due to mixing on the atomic level, are widely used in many industries such as ceramics, aerogels, dense films and fibers. Inorganic ion exchangers obtained by this synthesis approach could also produce the materials for drinking water treatment with higher surface reactivity and improved properties for toxic anions removal. However, traditional sol-gel synthesis cannot be defined as environmentally friendly due to the usage of expensive and toxic metal alkoxides as raw materials for synthesis as well as the final products are too expensive for water industries. The idea to develop inorganic ion exchangers via non-traditional sol-gel, in which, metal alkoxides would be replaced by simple inorganic salts as raw materials for the synthesis, was successfully realized few years ago and resulted in two new materials: layered Zn-Al and bulk Fe-Al hydrous oxides [1-2]. The next task has been to develop another layered double hydrous oxide, which would contain Mg in the composition instead of Zn. Fig. 1 shows the general approach of these new materials synthesis (a) and pure inorganic hydrogels of the recently developed Mg-Al hydrous oxides (b). These hydrogels (the

precursors of the layered Mg-Al hydrous oxide) obtaining is the main step of the synthesis approach.

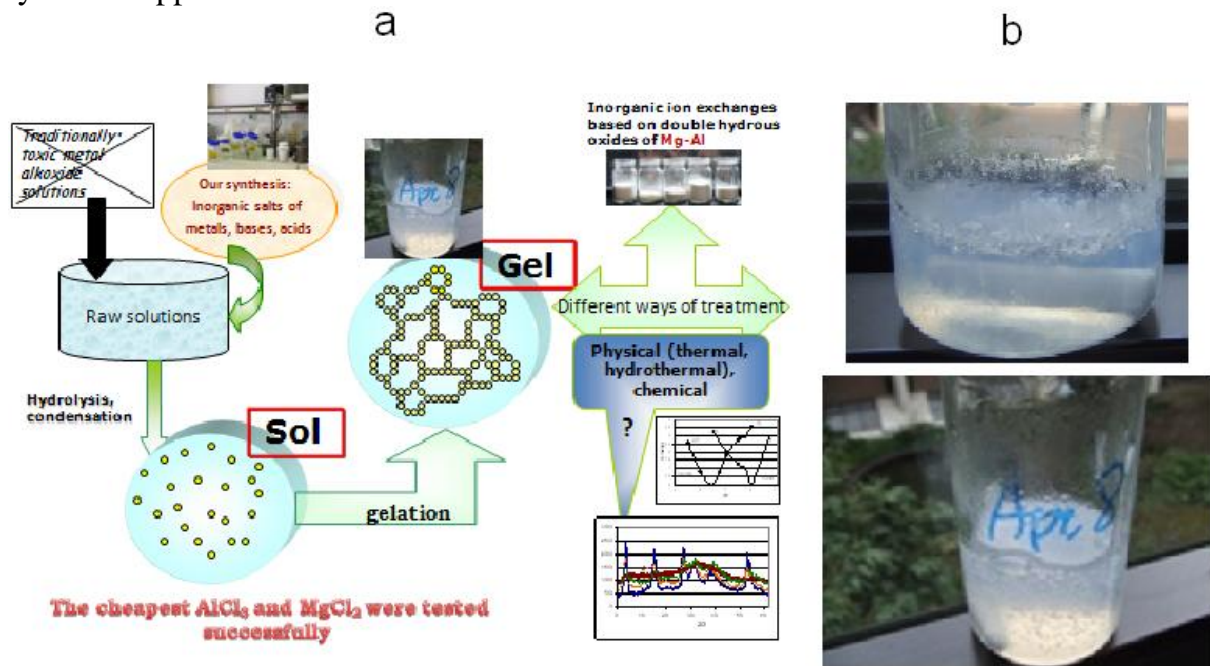


Fig. 1. Non-traditional sol-gel synthesis approach for production of Mg-Al double hydrous oxides (a) and pure inorganic hydrogels of Mg-Al hydrous oxides (b).

2.2 Characterization of the new materials structure and surface chemical properties

SEM and N₂ adsorption data (Fig. 2) show that the new Mg-Al hydrous oxides are highly porous materials with mesoporous structure and specific surface area ranged between 150-300 m²/g. XRD patterns of the developed Mg-Al hydrous oxides (Fig. 3, a) are typical for layered hydroxalcalite-type materials with high peaks at the lower values of 2Theta, however, the ratio of M²⁺:M³⁺ in the new Mg-Al hydrous oxide is 1:1 what is different as compare with naturally occurring hydroxalcalites. Taking into account that M²⁺ is Mg in the developed ion exchangers, this ratio (1:1) is a great advantage for arsenate removal task as the main competitor (phosphate) gets much lower uptake affinity as compare with arsenate due to this particularity of the chemical composition. FTIR spectra demonstrate that carbonate is the interlayer space anions (Fig. 3,b) with the characteristic vibrations at 1400-1800 cm⁻¹.

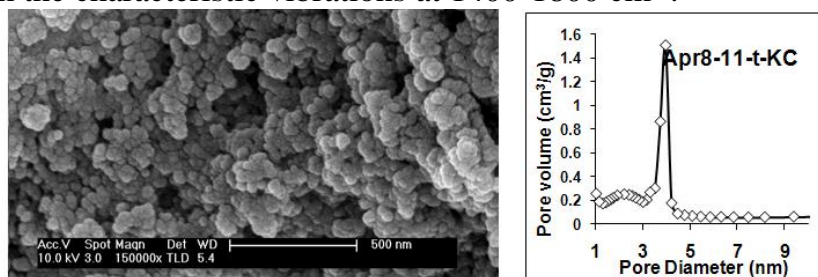


Fig. 2. SEM picture (left) and pore diameter data from N₂ adsorption studies (right) of the recently developed Mg-Al hydrous oxides.

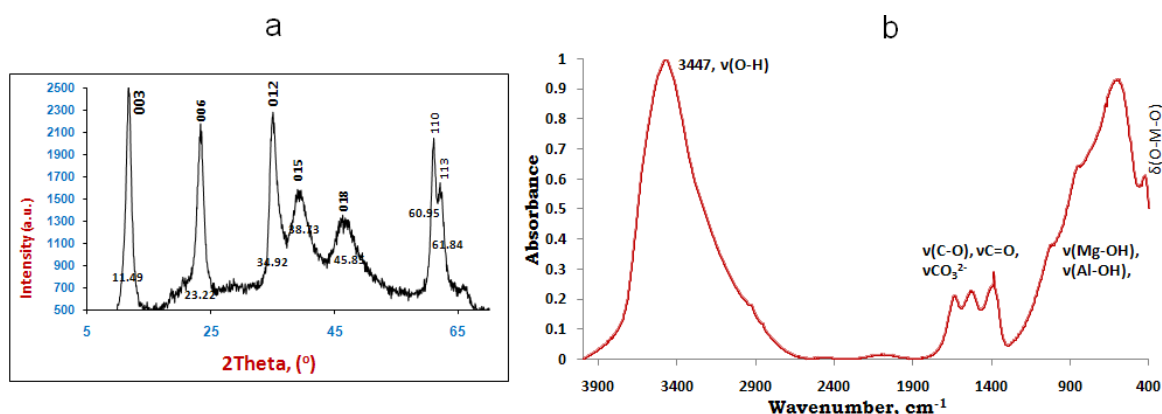


Fig. 3. XRD patterns (a) and FTIR spectra (b) of the new Mg-Al hydrous oxides.

Potentiometric titration data demonstrated exceptionally higher relative anion exchange capacity of the new Mg-Al hydrous oxide as compare with the previously developed Zn-Al oxides (Fig. 4, Ref. [1-2]), what correlates well with the adsorption of few anions shown below (Fig. 5).

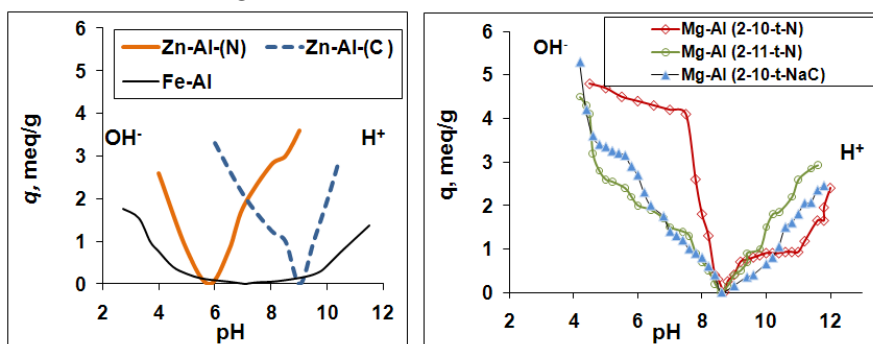


Fig. 4. Potentiometric titration curves of Zn-Al and Fe-Al hydrous oxides [1-2] (left) and differently treated the layered Mg-Al hydrous oxides (right).

2.3. Adsorptive affinity to target anions

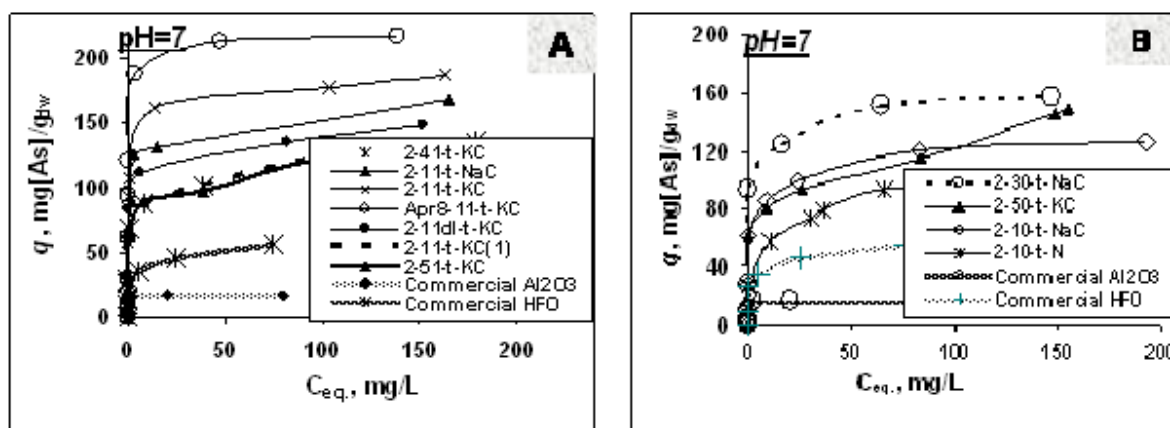


Fig. 5. Isotherms of H_2AsO_4^- adsorption onto layered hydrous oxide of Mg-Al obtained from xerogels (A) and directly from hydrogels (B) by different physico-chemical treatments. Conditions of the experiments: solids concentration: 2 g/L, background electrolyte: 0.1N NaCl, pH=7, temperature: 22 ± 2 °C, contact time: 72 hours.

New ion exchanger based on the layered hydrous oxides of Mg-Al demonstrated very higher adsorptive capacity and uptake affinity towards H_2AsO_4^- shown in Fig. 5.

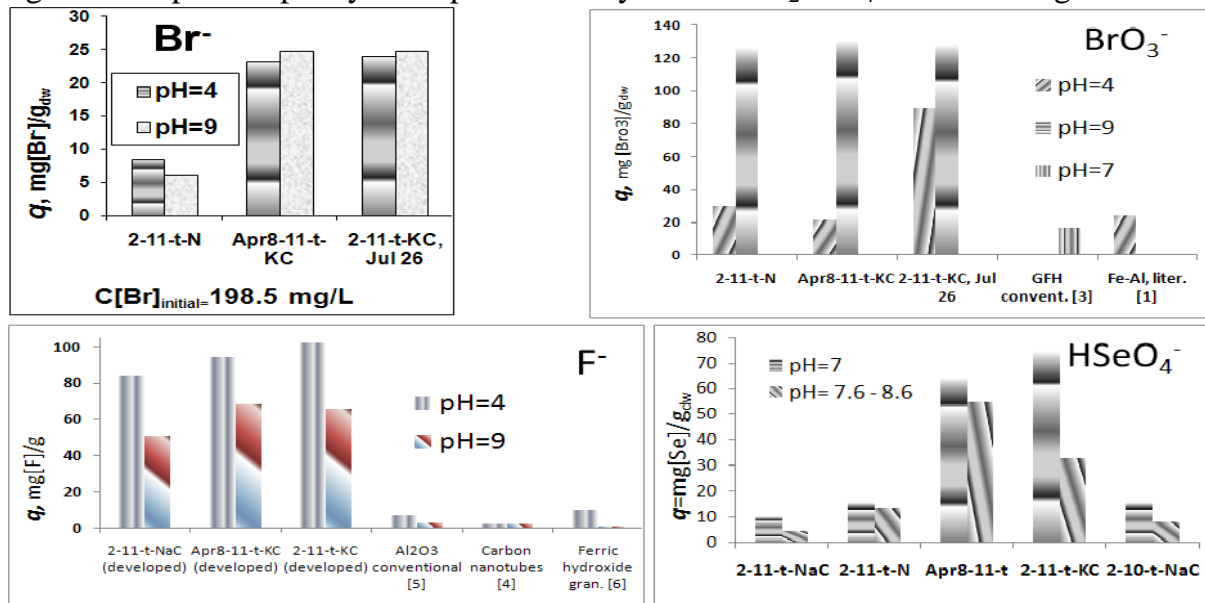


Fig. 6. Adsorption of Br^- , BrO_3^- , F^- and HSeO_4^- onto Mg-Al hydrous oxides at the initial concentration of these ions relatively: 198,5; 334,1; 212,0 and 127,2 mg/L at the adsorbent concentration : 2 g/L, background electrolyte: 0.1N NaCl, temperature: 22 ± 2 °C and contact time: 72 hours and comparison with the literature data.

3. DISCUSSIONS (short) AND CONCLUSIONS

It was previously noticed that (1) mixed hydrous oxides [1-2] had much attractive pH effect of sorption as well as that the layered mixed hydrous oxides had a very high affinity towards toxic arsenic compared to individual hydrous oxides [2]. In order to develop another layered mixed hydrous oxide, which would contain Mg instead of Zn in the composition, a new advanced method of synthesis was developed. The new method is non-traditional sol-gel synthesis, which avoids using toxic and expensive metal alkoxides as raw materials, what makes this synthesis method very cost-effective, environmentally friendly and technologically attractive (easy to run in ambient conditions and in larger scale).

The affinity of the new hydrous oxide of Mg-Al towards H_2AsO_4^- (steep isotherms) and the adsorptive capacity at pH=7 (the plateau at sorption isotherms) are the highest up to the moment and can reach 220 mg[As]/g_{dw} for the best sample. Less than 30 seconds is enough to reduce As(V) initial concentration of 10 mg/L up to zero. Higher removal ability for the other toxic anions (Br^- , BrO_3^- , F^- and HSeO_4^-) was also detected, Fig. 6. Uptake capacity of all Mg-Al hydrous oxides (obtained by any treatment of hydrogels) to As(III) was around 30-35 mg[As(III)]/g_{dw}.

Mechanism of As(V) adsorption was studied by EXAFS, FTIR and XPS and will be shown in the presentation. Briefly: mono- and bidentate coordinations of H_2AsO_4^- (depending on the way of hydrogel treatments) was detected by XPS. FTIR showed the involvement of the interlayer carbonate in the uptake process. EXAFS detected

As-Al bonds in the second coordination shell (not As-Mg).

Due to scientific, technological and ecological advantageous, the new cost-effective Mg-Al hydrous oxides are promising alternative of the anion exchanger for industrial scale application at drinking water treatment, first of all, for arsenic removal (and also for the other anions: F^- , Br^- , BrO_3^- , $HSeO_4^-$, As(III)) what was also documented by EU Patent application filled by Utrecht University on Sept. 14, 2010.

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