Removal of Manganese Content from Synthetic Aqueous Solution and Groundwater Using Direct Sonolysis/Hybrid Sonolysis

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This paper shows the results of laboratory scale tests for manganese removal from aqueous solutions and groundwater by sonolysis. Ultrasonic cavitation phenomena lead to active radicals generation able to transform soluble Mn (II) into insoluble species. The influence of initial manganese concentration, sonolysis time, oxidant (H_2O_2) and catalyst doses (Fe) in case of hybrid sonolysis, energy and amplitude of ultrasonic waves on manganese removal have been studied. Three categories of ultrasonic test were performed for synthetic solutions: direct sonolysis (US), hybrid system US + H_2O_2, Fenton sonolysis US + H_2O_2 + Fe. Based on preliminary results Fenton sonolysis was selected for experimental with groundwater (280 μg Mn/L, 180 μg Fe initial / 1200 μg Fe/L after addition of ferrous sulfate, 12 mg C/L - dissolved organic carbon). Residual manganese concentration was 40 μg Mn/L, below the limit (50 μg Mn/L) for drinking water. The real pollution matrix of groundwater changes the optimal operational conditions significantly so, must be taking into consideration local characteristics during the year.

Keywords: cavitation, groundwater, manganese, sonolysis, ultrasonic

Manganese II and IV are dominant species in aquatic environment and the concentration levels in non-polluted waters (soluble phase) could be 10 – 1000 μg Mn/L but, usually are below 200 μg Mn/L [1,2]. The most present compounds are: $MnCl_2$, $MnSO_4$, Mn_3O_4 (hausmanite), MnO_2 (pyrolusite), $KMnO_4$, $C_9H_7MnO_3$ (MMT – additive for fuels) (WHO, 2004) [3,4].

The radical mechanism (hydroxyl radicals generation because of ultrasonic cavitation effect) is typical for Advanced Oxidation Processes from which sonolysis and hybrid sonolysis can be a part.

Sonolysis is a well-known water treatment method for organics oxidation and disinfection but in the field of inorganic load diminishing are very few mentions [5].

Similar to ordinary sonic waves, ultrasonic radiation passing throw the water and generates compressing-decompressing cycles inside the solution. At some point the energy of decompressing phase becomes higher than molecular attraction forces and cavitation will appear into solution volume. This phenomenon is the base of chemical effect of ultrasonic field because of active radicals (e.g. hydroxyl radicals •OH) formation in specific cavitation conditions (high pressure and temperature) [5,6].

Literature data mentions the following possible reactions under the influence of ultrasonic field:

$H_2O + US \rightarrow \bullet OH + H\bullet$

$2H_2O + US \rightarrow 2\ HO^- + H_2$

$Mn(II) + \bullet OH + HO^- \rightarrow Mn(OH)_2$

Manganese could be replacing the iron and might inhibit chlorophyll synthesis but generally it is a microelement useful for ecosystem below specific concentration limits.

Manganese concentration levels from groundwater (≤ 1.3 mg Mn/L) are higher than surface waters. In humans, the frequently exposure to manganese is food 0.7-10.9 mg Mn/day (higher in case of vegetarians). Body tissues, leaver, kidneys have manganese content and might be accumulated in children's brain. *Manganism* is a disease caused by excessive manganese consumption (including by smoking) with symptoms very similar with Parkinson illness [4].

Drinking water treatment plants with groundwater sources have a treatment phase for manganese and iron removal in order to prevent this risk for human health. Aeration and filtration (sand/manganese coated sand) are the most used processes for this. In case of higher manganese content (1.3 mg/L) some oxidants must be adding (permanganate, chlorine, hydrogen peroxide) [7].

This paper shows the possibility to use ultrasonic field for manganese removal from aqueous systems.

Experimental part

Reaction total time, sonolysis time, initial manganese concentrations, energy and amplitude of ultrasonic waves, oxidant (hydrogen peroxide) and catalyst (Fe^{2+}) doses were the main operating parameters which were studied:

-sonolysis time: 5÷60 min;
-initial manganese concentration: 86-645 μg Mn/L;
-ultrasonic energy: 1 x 10^6 – 8 x 10^6 J;
-ultrasonic amplitude: 20 – 100%;
-catalyst dose: 1.7 – 6 mg Fe^{2+}/L;
-oxidant dose: 640 – 2000 mg H_2O_2/L.

Sonics – Vibracell VCX 500 was the ultrasonic generator working on the stable 20 kHz frequency for all experimental tests.

Four sonolysis systems were tested: direct sonolysis US; US + H_2O_2, US + H_2O_2 + Fe^{2+} (Fenton sonolysis) and US + H_2O_2 + Fe^{2+} + UV (photo-Fenton sonolysis).

pH of aqueous model solutions was 7 – 8 with different manganese concentrations, NaOH being used for *p*H correction taking into account the decrease because of $MnSO_4$ adding.

Two sonolysis systems were selected for real groundwater treatment (find to be optimal after preliminary tests):

a)US + H_2O_2 + Fe^{2+}: 280 μg Mn/L, 1200 μg Fe/L, 1280 mg H_2O_2/L, 30 min. ultrasonication;

b)US + H_2O_2: 280 μg Mn/L, 180 μg Fe/L (from initial groundwater), 1280 mg H_2O_2/L, 30 min. ultrasonication.

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No.	Sample	Energy, Joule	Amplitude, %	Time, min.	Initial, μg Mn/L	Final, μg Mn/L
1	U1	4x10⁶	25%	5	170	145
2	U2			15		125
3	U3			30		126
4	U4			45		159
5	U5			60		165

Table 1
INFLUENCE OF SONOLYSIS TIME TO MANGANESE RESIDUAL CONCENTRATIONS

Initial groundwater characteristics were as following: *p*H = 7.4, conductivity 536 μS/cm, NH_4^+ 0.3 mg/L, total iron 179 μg/L, manganese 280 μg/L, dissolved organic carbon (DOC) 11.4 mg/L.

Results and discussions

Preliminarily direct sonolysis tests

Elementary tests were performed for aqueous synthetic solutions with manganese content in order to establish the optimal operating parameters.

Sonolysis time influence

Sonolysis time is an important parameter both for cavitation process and economic aspect (a shorter sonolysis time leads to less expensive energy costs). Table 1 shows the time influence to residual manganese concentration levels. The removal efficiencies are presented in figure 1. Maximum value 26% was for 15 – 30 min.

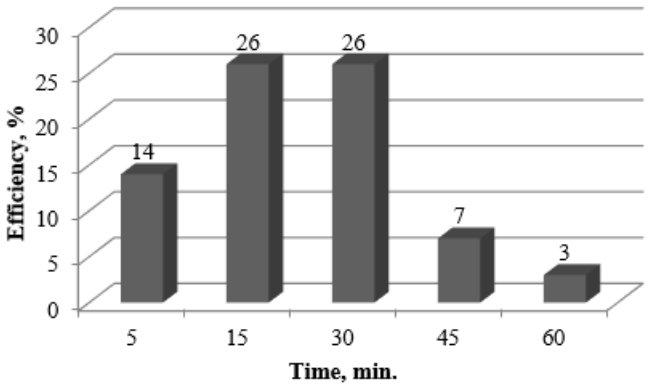

Fig. 1.Evolution of manganese removal efficiencies relative to ultrasonication times

The increase of sonolysis time over 30 min led to the decrease of manganese removal efficiency probably because the manganese precipitates particles size become below 20 μm (filtration membrane). Removal efficiency was maximum 26% for manganese initial concentration ≤ 170 mg Mn/L

The influence of initial manganese concentration

The sonolysis tests with different manganese concentration levels had the main goal, to test the limit of the method and to establish the concentration domain were the sonolysis is efficient. Four different initial manganese were tested and the residual levels are shown in table 2.

Residual manganese concentrations (~ 65 mg Mn/L) are almost the same if initial concentration is below 120 mg Mn/l but the efficiency has maximum value 46% for initial manganese concentration of 120 g Mn/L.

The influence of ultrasonic energy

The ultrasonic wave energy is another parameter of sonolysis which can influence the process efficiency. The experimental test were done for 464 mg Mn/L solution in order to improve the efficiency for higher initial manganese content.

Our tests were performed for 25% amplitude and 15 minute ultrasonication time. Table 3 and figure 2 emphasizes the evolution of manganese residual concentrations and removal efficiencies for four different values of ultrasonic wave energy.

The results show that increasing of energy doesn't the effect of rising manganese removal yield. The maximum value was 25% for 4 x 10^6 J.

The influence of ultrasonic amplitude

Experimental tests were performed for 464 μg Mn/L concentration and 4 x 10^6 J energy.

Six different amplitudes were studied and the results

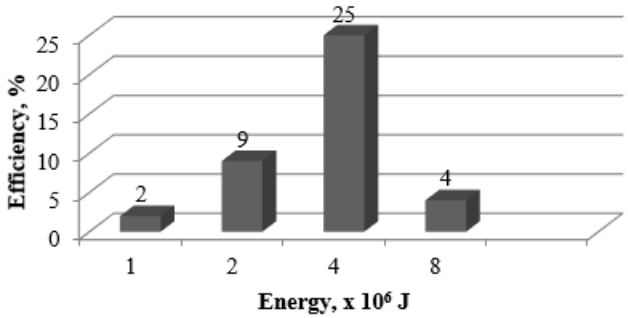

Fig. 2.Evolution of manganese removal efficiencies relative to energy of ultrasonic waves

No.	Sample	Energy, Joule	Amplitude, %	Time, min.	Initial, μg Mn/L	Final, μg Mn/L
1	U6	4x10⁶	25%	15	86	66
2	U7				120	65
3	U2				170	125
4	U9				464	348

Table 2
INFLUENCE OF MANGANESE INITIAL CONCENTRATIONS

No.	Sample	Energy, Joule	Amplitude, %	Time, min.	Initial, μg Mn/L	Final, μg Mn/L
1	U10	1x10⁶	25%	15	464	453
2	U11	2X10⁶				424
3	U9	4X10⁶				348
4	U12	8X10⁶				447

Table 3
INFLUENCE OF WAVE ENERGY

No.	Sample	Energy, Joule	Amplitude, %	Time, min.	Temp., ^{0}C	After, μg Mn/L
1	U13	4x10^6	20	15	30	418
2	U14		30		30	436
3	U15		40		35	455
4	U16		60		45	366
5	U17		80		58	320
6	U18		100		65	302

Table 4
INFLUENCE OF WAVE AMPLITUDE

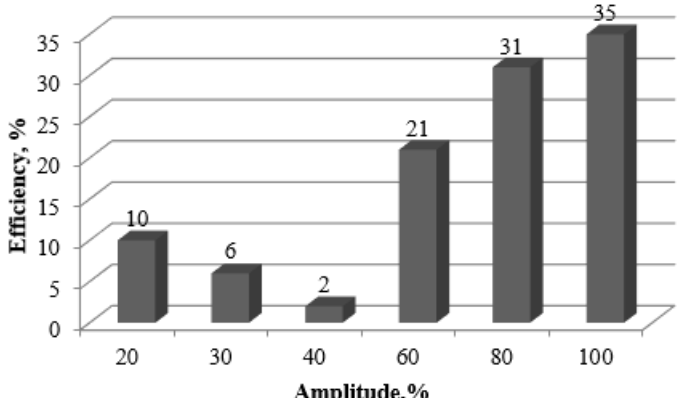

Fig. 3. Evolution of manganese removal efficiencies relative to amplitude of ultrasonic waves

No.	Sample	Energy, Joule	Amplitude., %	Time, min.	Initial Fe, μg/L	Initial Mn, μg/L	Final Mn, μg/L	ηMn, %
1	U19	4x10^6	80	15	800	617	512	17
2	U20				1200	645	264	59
3	U21				2400	855	598	30

Table 5
INFLUENCE OF CATALYST DOSE

No.	Sample	Energy, Joule	Amplitude, %	Time, min.	Dose H_2O_2, mg/L	Initial Fe, μg/L	Initial Mn, μg/L	Final Mn, μg/L	ηMn, %
1	O1	8x10^6	80	30	2130	-	644	44	93
2	O2				1704			154	76
3	O3				1278			121	81
4	O4				639			129	80
5	O5				1278	1200		92	86
6	O6				639	1200		182	72

Table 6
INFLUENCE OF OXIDANT DOSE

are shown in table 4 and figure 3.

The removal efficiency of manganese growth to over 30% in case of higher amplitudes (≥ 60%) for the initial concentration similar to previous tests - 464 μg Mn/L.

The influence of iron catalyst on direct sonolysis

Iron (II) is well known as a catalyst in Fenton – like Fenton oxidation processes having an important role in hydroxyl radicals generation.

This role was highlighted in the sonolysis system US + $FeSO_4$. Three different iron (II) doses were added to the water samples together with ultrasonic field application for 15 min. Higher levels of manganese content were selected in order to find the maximum removal efficiency

The residual manganese, iron concentrations and manganese removal efficiencies were emphasized in table 5.

In case of 645 μg Mn/L the removal efficiency was maximum ~60% (for iron dose 1200 mg Fe/L) but residual manganese was over admitted limit for drinking water.

The influence of hydrogen peroxide on direct and Fenton sonolysis

Sonolysis tests in the presence of hydrogen peroxide (639 – 2130 mg H_2O_2/L) and iron catalyst were performed. Na_2SO_3 was add as activ oxigen scavenger to the end of tests in order to stop the oxidation after 30 min. Table 6 shows experimental conditions and manganese removal efficiency.

Hybrid sonolysis with hydrogen peroxide and iron has proved to be the most efficient method for oxidation and precipitation of manganese (ηMn = 72 – 93%) (reaction time 30 min. was increased in order to have time for hydrogen peroxide reaction).

Manganese removal from groundwater by hybrid sonolysis

Two sonolysis systems were chosen for the treatment of groundwater with manganese content:

System US + H_2O_2: initial manganese concentration 280 μg Mn/L, iron concentration 180 μg Fe/L (natural content), hydrogen peroxide concentration 1278 mg H_2O_2/L, sonolyse time 30 min, amplitude 80%, energy 8x10^6 J.

System US + H_2O_2 + Fe: initial manganese concentration 280 mg Mn/L, iron concentration 1200 mg Fe/L, hydrogen peroxide concentration 1278 mg H_2O_2/L, sonolyse time 30 minutes, amplitude 80%, energy 8x10^6 J.

These operating conditions were selected based on previous laboratory tests.

The main characteristics of groundwater were: *p*H = 7.4, conductivity = 536 μS/cm, NH_4^+ = 0.3 mg/L, Fe = 180 mg/L, Mn = 15.1 mg/L, DOC = 11.4 mg/L.

Manganese was removed ~70 % (residual manganese content 84 mg Mn/L over the admitted limit) using the hybrid system US + H_2O_2 + Fe comparing with ~ 20% (residual manganese content 224 μg Mn/L) in case of US + H_2O_2 witch proved that iron catalyst is an important factor. The increase of hydrogen peroxide dose with 20% leads to 40 μg Mn/L in the treated water by US + H_2O_2 + Fe system (below admitted limit).

Conclusions

The experimental tests revealed the main parameters which control the direct and hybrid sonolyse of water with manganese content. Preliminary tests with synthetic manganese solutions emphasized the role of ultrasonic field characteristics (energy, amplitude), sonolysis time, manganese initial concentration, oxidant (hydrogen peroxide) and catalyst (ferrous sulphate) concentrations on removal effficiencies.

The best selected operating conditions were applied to sonolitic test with underground water. Hybride catalysed sonolysis US + H_2O_2 + Fe has proved to be the best option to remove manganese to ~ 70% efficiency (residual manganese below admitted limit of 50 μg Mn/L) for 280 μg Mn/L initial content. It is recommended to take into consideration the entire pollution matrix of groundwater because its influence on oxidant applied dose (higher doses in case of oxidant scavenger compounds).

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