

REMOVAL OF SELECTED HEAVY METALS (LEAD AND CADMIUM) FROM AQUEOUS SOLUTIONS USING IONIZING RADIATION

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Abstract

The paper describes possibilities of irradiation for the removal of lead and cadmium ions presented in aqueous solutions both separately and together at different initial concentrations. The effect of radiation dose applied, various gases for deoxygenation of solution as well as of different scavengers of OH radicals was in detail investigated. The conditions leading to the effective radiation reduction and precipitation of both metals have been found.

Introduction

Among the various contaminants contained predominantly in industrial wastewater the toxic heavy metals belong to the most dangerous ones. Therefore, their removal before the recycling or releasing of wastewater to the environment appears to be one of the most actual tasks. As an alternative process to the conventional chemical methods, ionizing radiation may be successfully utilized for the reduction of numerous metal ions to insoluble metals. This application is generally based on the gradual reduction of ions (Me^{x+}) by the primary reducing products of water radiolysis (solvated electrons e_{aq}^- and H radicals) up to the metallic form. However, the reoxidation of final metal Me, and intermediates by primary oxidizing species (OH radicals, H_2O_2) as well as by dissolved oxygen has to be prevented. Therefore, the presence of appropriate OH radical scavengers appears to be indispensable. It was demonstrated [1] that at a dose of 40 kGy 96 % of Pb^{2+} ions may be removed by electron beam irradiation (EB) from 10^{-3} mol/l of PbCl_2 solution using an ethanol additive. In the presence of sodium formate, the complete removal of Pb^{2+} ions from aerated solutions containing 10-20 mg Pb^{2+} /l was attained at a dose of 1,2 kGy [2]. As it follows from some pulse radiolysis studies [3-5], many factors may substantially affect not only kinetics and mechanism of elemental reactions but also the efficiency of the whole radiation process including the precipitation of metals. This research was focused on the lead and cadmium ions presented in aqueous solutions both separately and together at different initial concentrations and on the search for the optimum conditions for their removal. Both EB and gamma radiation were applied. The air-saturated solutions and those deoxygenated by various gases were irradiated. The effect of different scavengers was investigated in detail.

Experimental

The following series of different soluble salts (chloride, nitrate and acetate of lead, for cadmium nitrate only) were irradiated:

- solutions with variable initial concentration (c_0) of metal ranging from 20 to 200 mg dm^{-3} containing the admixture of 10^{-2} mol dm^{-3} potassium formate
- solutions as a), deaerated by means of bubbling (15-20 min) with N_2 , H_2 and helium
- solutions as a) containing instead of HCOOK the 1 and 10 vol.% admixture of aliphatic alcohol scavengers (methanol, ethanol, 2-propanol and isobutyl alcohol)
- solutions as a), saturated by nitrous oxide
- solutions as c), saturated by nitrous oxide

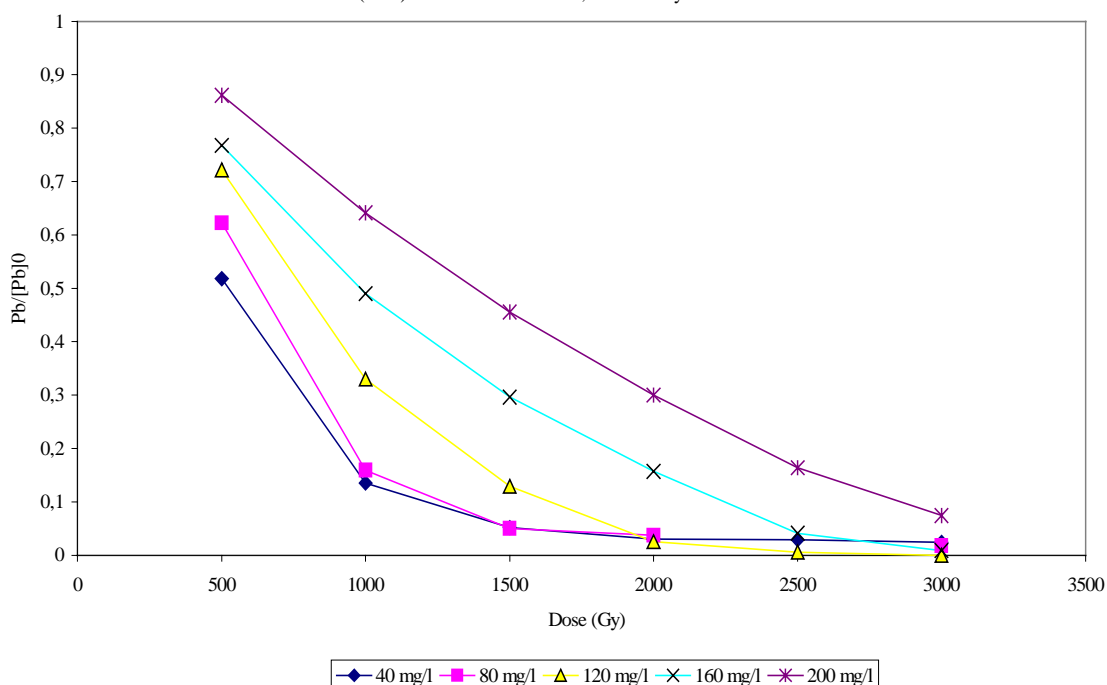
f) solutions containing together both metals in the form of nitrate in different ratios.

The samples were irradiated in sealed thin-glass ampoules with ^{60}Co gamma rays (dose rate D' of $17,4 \text{ Gy h}^{-1}$) and by accelerated electrons $4,5 \text{ MeV}$ ($D' = 0.5\text{-}1,5 \text{ Gy s}^{-1}$) at the doses ranging from 2 to 40 kGy. The Fricke and polymethylmetacrylate dosimeters were used for the dose estimation, respectively. The changes in metals concentration were determined (with the error of $\pm 5\%$) by means of atomic absorption spectroscopy with flame atomization. After exposure the ultrafiltration with Milipore filter ($0,45 \mu\text{m}$ pore size) in the flow of nitrogen or centrifugation (21 400 g) were used for the separation of the product- finely dispersed metallic particles.

Results and discussion

The preliminary experiments showed that both mentioned ways of separation are quite equivalent so that the standard centrifugation was used. In the absence of the OH radical scavengers no radiation reduction takes place under given conditions. As it follows from Fig. 1, the lead at $c_0 = 100 \text{ mg/l}$ may be complete removed from non-deaerated solutions already at a dose of $2,5 \text{ kGy}$ using a HCOOK as OH radicals scavenger regardless of the sort of anion. Under identical conditions the cadmium requires dose of 12 kGy to be totally reduced.

Figure 1: Dependence of normalized Pb^{2+} concentration on the dose for different initial concentrations. System $\text{Pb}(\text{NO}_3)_2 + 10\text{-}2 \text{ mol/l HCOOK}$, irradiated by electron beam



Ion HCOO^- appears to be very effective scavenger of OH radicals:

$\text{HCOO}^- + \text{OH} \rightarrow \text{COO}^- + \text{H}_2\text{O}$. Ionradical COO^- reduces both Me^{2+} ions and intermediate ions (Me^+). $\text{Me}^{2+} + \text{COO}^- \rightarrow \text{Me}^+ + \text{CO}_2$, $\text{Me}^+ + \text{COO}^- \rightarrow \text{Me} + \text{CO}_2$. Moreover in non-deaerated solutions it reduces the concentration of oxygen:

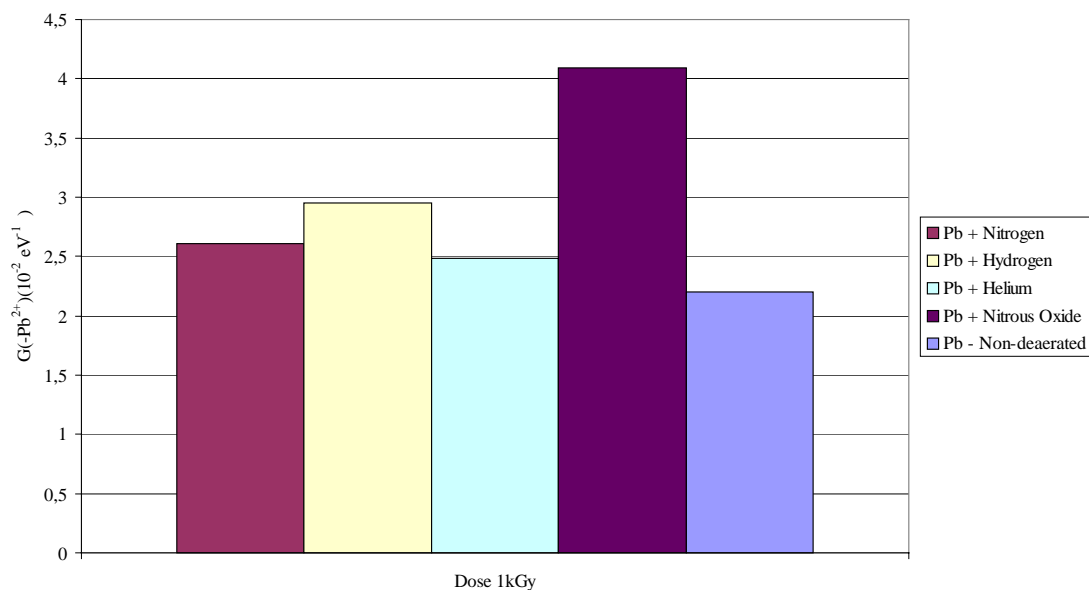
$\text{COO}^- + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}_2^-$. The dominant reducing species are primary products of the water radiolysis e_{aq}^- and H radicals: $\text{Me}^{2+} + e_{\text{aq}}^- \rightarrow \text{Me}^+$. For lead the following reactions take place: $\text{Pb}^+ + \text{H} \rightarrow \text{PbH}^+$,

$\text{Pb} + \text{Pb}^+ \rightarrow \text{Pb} + \text{Pb}^{2+}$, $\text{PbH}^+ + \text{PbH}^+ \rightarrow \text{Pb} + \text{Pb}^{2+} + \text{H}_2$ and for cadmium $\text{Cd}^+ + \text{Cd}^+ \rightarrow \text{Cd} + \text{Cd}^{2+}$,

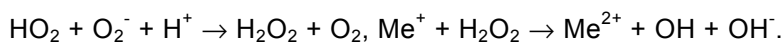
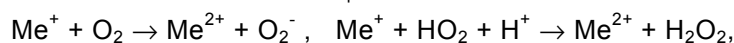
$\text{Cd}^+ + \text{Cd}^+ \rightarrow \text{Cd}_2^{2+}$, $\text{Cd}_2^{2+} \rightarrow \text{Cd} + \text{Cd}^{2+}$ The rate constants of all these reactions are very high ($10^8\text{-}10^9 \text{ l mol}^{-1} \text{ s}^{-1}$) whereas the reaction $\text{Me}^{2+} + \text{H} \rightarrow \text{Me}^+ + \text{H}^+$ is for cadmium slow and with lead it does not proceed [4].

In accordance with the reductive mechanism of the process the deaeration of solution increases the reduction yield $G(-\text{Pb}^{2+})$, Fig. 2.

Figure 2: Radiation yields $G(-Pb^{2+})$ for the system $Pb(NO_3)_2$, $c_0 = 100 \text{ mg/l} + 10^{-2} \text{ mol/l HCOOK}$, irradiated by EB



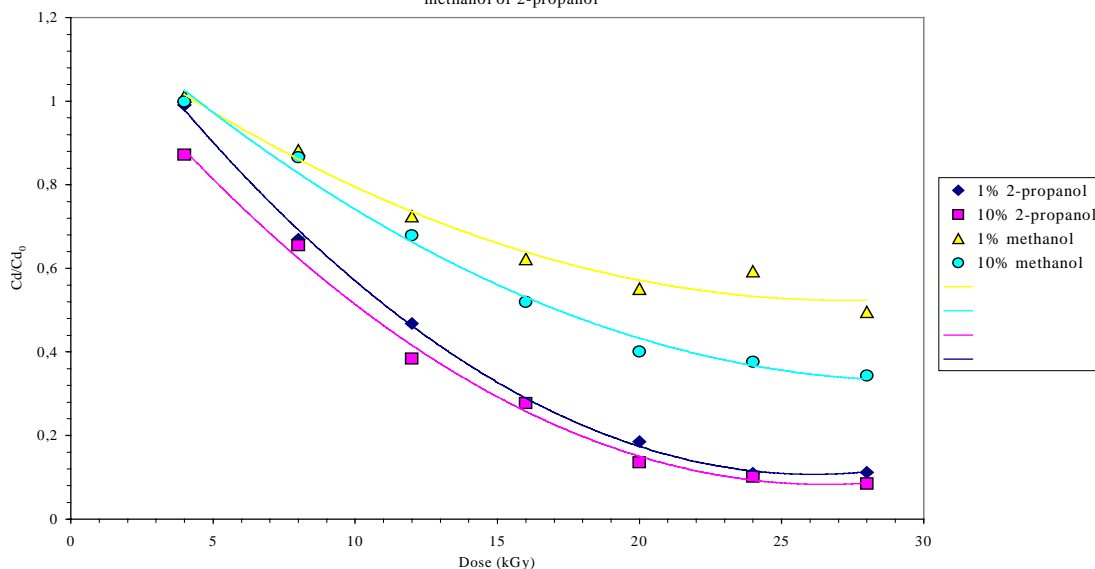
The aereal oxygen reduces the concentration of both reducing species (e_{aq}^- and H atoms) and oxidizes ions Me^+ : $O_2 + e_{aq}^- \rightarrow O_2^-$, $O_2 + H \rightarrow HO_2$, $O_2^- + H^+ \leftrightarrow HO_2$



In addition to the positive effect of hydrogen the pronounced increase of G value was observed with the Pb^{2+} solution saturated by nitrous oxide. This gives evidence for its participation in mechanism of radiation process. No analogous effect was found with cadmium, where N_2O oxide acts only as deaerating agent, comparable with others gases.

Unlike the formate, the complete reduction of Me^{2+} ions in the environment of aliphatic alcohols requires doses achieving several tens of kGy, being still higher for cadmium (Fig. 3).

Figure 3: Normalized concentration of Cd^{2+} ions vs. dose of EB radiation. System $Cd(NO_3)_2 + 1$ and 10 vol% of methanol or 2-propanol



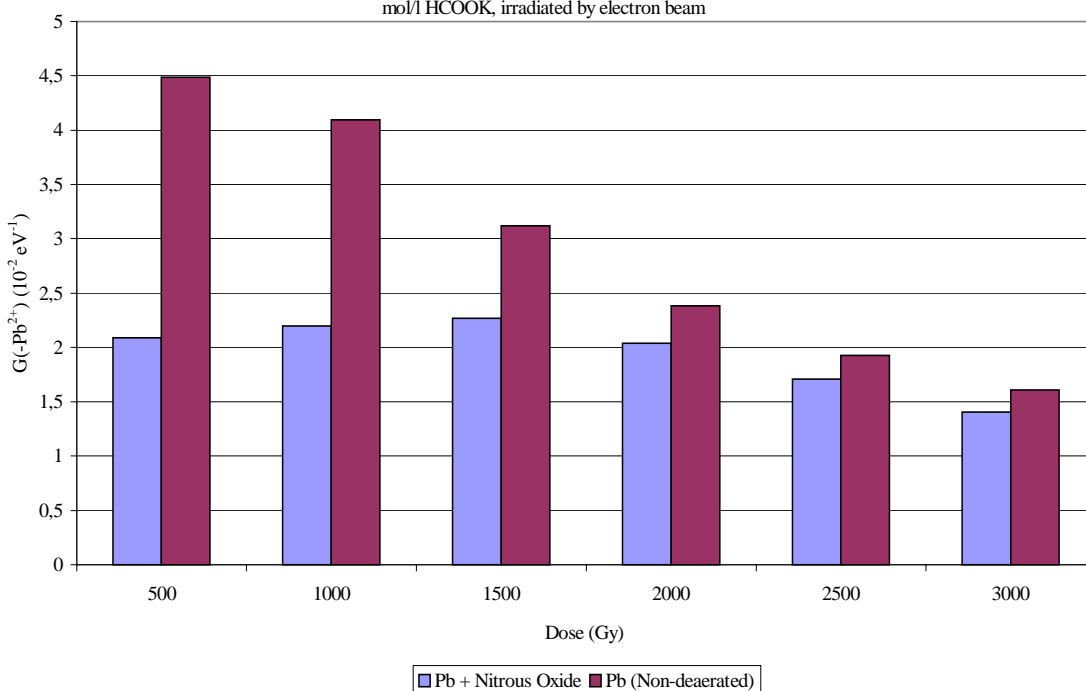
The effectiveness of individual alcohols was found to be very different (Table 1) and dependent on concentration. Therefore, their amount should be optimized.

Table 1: Radiation yields $G(-Pb^{2+})$ and $G(-Cd^{2+})$ [$10^{-2} eV^{-1}$] for 10 vol.% addition of different alcohol scavengers

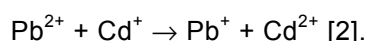
Scavenger	$G(-Pb^{2+})$ Dose 8 kGy	$G(-Cd^{2+})$ Dose 16 kGy
2-propanol	0.38	0.38
Isobutanol	0.31	-
Methanol	0.29	0.32
Ethanol	0.25	0.22

The radiation yield $G(-Pb^{2+})$ in the system containing formate may be markedly increased by saturation of solution with nitrous oxide (Fig.4). This positive effect decreases with dose, which is quite general trend giving evidence for the recombination processes. For Cd^{2+} ions this effect was found to be zero. On the contrary in the presence of alcohol scavengers only negative effect was found for both metals.

Figure 4: Dependence of normalized Pb^{2+} concentration on the dose for the system $Pb(NO_3)_2$, $c_0 = 100 \text{ mg/l} + 10^{-2} \text{ mol/l HCOOK}$, irradiated by electron beam

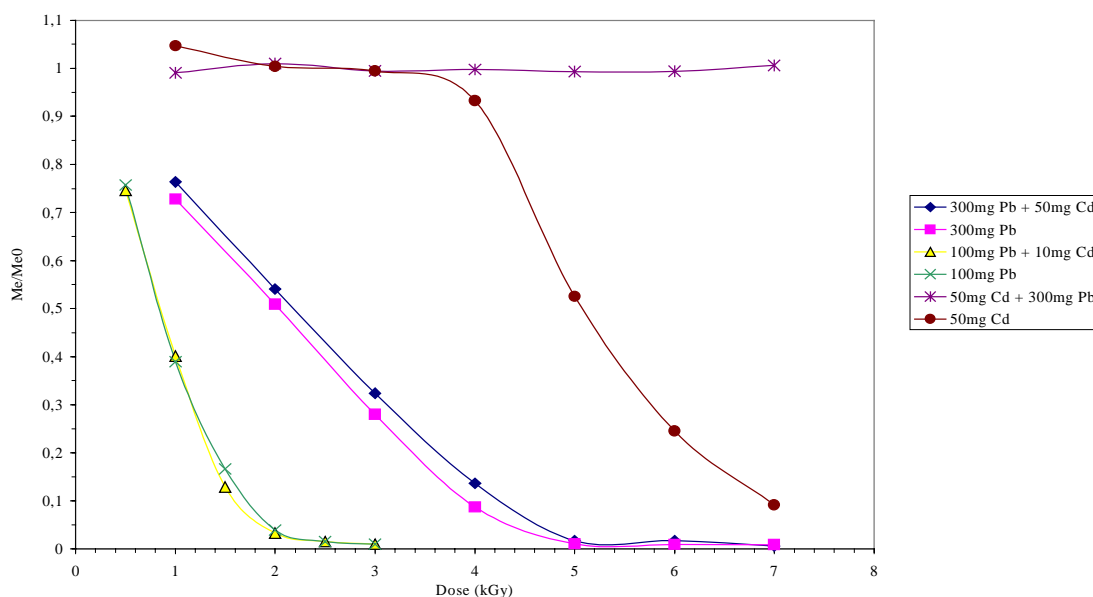


As it follows from Fig. 5, in the mixture containing both metals in different ratios, the Pb^{2+} ions are reduced independently of the presence of cadmium, whereas the reduction of Cd^{2+} ions takes place after the total reduction of lead ions. The rate constants of the reaction $Me^{2+} + e_{aq}^- \rightarrow Me^+$ are similar for both metals, therefore e_{aq}^- react with both metallic ions. In the following step the originating Cd^+ ions interact with Pb^{2+} ions:



The kinetics and actual degree of radiation reduction are different for both types of radiation applied (gamma rays or accelerated electrons) differing by some orders in the dose rate. These differences increase with increasing dose and may be connected with the way of radiation energy deposition in the substrate. Therefore, various partial reactions including recombination processes assert during the reduction in the different extent.

Figure 5: Dependence of normalized Pb^{2+} and Cd^{2+} ions concentration on the dose of EB radiation for the mixture of both metals in different ratios



Conclusions

- The lead and cadmium with initial concentration from 20 to 200 mg/l may be completely removed from aqueous solutions containing an addition of potassium formate (pH= 5-6) using accelerated electrons or gamma rays at doses of several units.
- The efficiency of radiation reduction increases with the solutions deaerated by inert gases or hydrogen and with the Pb^{2+} ions it may be increased by about 80% in the solution saturated with nitrous oxide.
- Radiation reduction by secondary radicals resulting in the reaction of OH radicals with the aliphatic alcohols requires for complete precipitation of both metals higher doses achieving several tens of kGy. The process is dependent on the concentration of individual alcohol scavenger.
- In the solutions containing both metals together the observable reduction of Cd^{2+} ions begins after the total reduction of lead ions.

Acknowledgements

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References

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