Removal of heavy metals from water by electron-beam treatment in the presence of an hydroxyl radical scavenger

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Electron-beam treatment in combination with the use of formate as an hydroxyl radical scavenger and subsequent filtration has been developed for the removal of heavy metals (cadmium, lead, chromium) from water.

One of the most important environmental problems is the removal of heavy metals from waste water. We used an electron-beam technique, which is applicable for the purification of various waste waters, (see *e.g.* refs. 1–4) to remove these metals from the water. The method is based on radiation-chemical reduction of the metal ions to their respective metals or to lower oxidation state ions which can then be removed by filtration. Two requirements are necessary: the absence of oxygen in the water (in the case of Cd^{II} and Pb^{II}) and scavenging of OH radicals which can oxidize the reduced metal ions.

The reduction, upon electron-beam treatment, can be a result of reactions of the ions with hydrated electrons e^-_{aq} and H atoms formed from water radiolysis.[5] For example, in the case of Cd^{II} ions, it is possible to write:

$$Cd^{II} + e^-_{aq} \longrightarrow Cd^{I} \tag{1}$$
$$Cd^{II} + H \longrightarrow Cd^{I} + H^+ \tag{2}$$
$$Cd^{I} + Cd^{I} \longrightarrow Cd^{II} + Cd^0 \tag{3}$$

If the water is saturated with air, oxygen reacts with e^-_{aq} and H [equations (4)–(6)], partially or completely suppressing reactions

$$e^-_{aq} + O_2 \longrightarrow O_2^- \tag{4}$$
$$H + O_2 \longrightarrow HO_2 \tag{5}$$
$$HO_2 \rightleftharpoons H^+ + O_2^- \tag{6}$$

(1) and (2). Since the reactions of HO_2 and O_2^- with Cd^{II} and Pb^{II} are comparatively slow, upon electron-beam treatment they can combine forming hydrogen peroxide:

$$HO_2 + O_2^- + H^+ \longrightarrow H_2O_2 + O_2 \tag{7}$$

and/or react with reduced metal ions:

$$Cd^{I} + HO_2 + H^+ \longrightarrow Cd^{II} + H_2O_2 \tag{8}$$

Hydrogen peroxide can also oxidize such ions:

$$Cd^{I} + H_2O_2 \longrightarrow Cd^{II} + OH + OH^- \tag{9}$$

The reduction takes part after the consumption of oxygen, and so to decrease the required dose air should be removed from water (for example, by bubbling inert gas) before and/or during electron-beam treatment.

Hydroxyl radicals formed from water radiolysis and in reaction (9) react with reduced ions:

$$Cd^{I} + OH \longrightarrow Cd^{II} + OH^- \tag{10}$$

In the case of Pb^{II} ions, hydroxyl radicals can react with them forming Pb^{III} (see *e.g.* ref. 5):

$$Pb^{II} + OH \longrightarrow Pb^{III} + OH^- \tag{11}$$

Then reaction (12) can proceed:

$$Pb^{III} + Pb^{I} \longrightarrow 2Pb^{II} \tag{12}$$

Hydrogen peroxide is also a water radiolysis product; together with the H_2O_2 produced from reactions (7) and (8) it can oxidize reduced ions. The overall effect will be that the metal ions will not be reduced to the free metal.

To exclude the negative influence of hydroxyl radicals it is possible to use a scavenger which converts the hydroxyl radicals into reducing species. Such a scavenger is formate ion. In reaction with hydroxyl radicals it gives COO^- radical ion which can then reduce metal ions:

$$HCOO^- + OH \longrightarrow COO^- + H_2O \tag{13}$$
$$Cd^{II} + COO^- \longrightarrow Cd^{I} + CO_2 \tag{14}$$
$$Cd^{I} + COO^- \longrightarrow Cd^0 + CO_2 \tag{15}$$
$$COO^- + O_2 \longrightarrow CO_2 + O_2^- \tag{16}$$

The carbon dioxide produced in reactions (14)–(16) is not toxic, yet the use of other hydroxyl radical scavengers can give rise to the formation of toxic compounds. For instance, ethyl and isopropyl alcohols which are also utilized as scavengers can form acetaldehyde and acetone, respectively. In addition, $R\dot{C}HOH$ radicals formed can oxidize Cd^{I}.

We studied the removal of cadmium, lead and chromium from model aqueous solutions. The first two metals were initially in the form of bivalent ions, and chromium was in the form of a chromate ion. Cd^{II} and Pb^{II} were reduced to Cd^0 and Pb^0, and Cr^{VI} was reduced to Cr^{III}.

The source of the ionizing radiation was a linear U-12 electron accelerator (electron energy 5 MeV, pulse duration 2.3 μs). Doses were measured with an ordinary or modified Fricke dosimeter (in a dependence on dose rate).[6] The total dose was varied by changing the amount of electron pulses or by changing the irradiation duration when a series of pulses (400Hz) were used. The concentrations of cadmium and lead were determined using a Perkin-Elmer 'Plasma-40' atom absorption spectrometer. Analysis of Cr^{VI} was performed spectrophotometrically from the optical density of the solution at 373nm (pH 10–11, molar extinction coefficient 461 $m^2\ mol^{-1}$,[7,8] the solution was filtered if Cr^{III} hydroxide precipitate was formed) using a 'Specord M-40' spectrophotometer. All reagents were analytical grade. The solutions were aerated and deaerated. The removal of air from the solutions was conducted by bubbling purified argon for 30–40min. The precipitates formed upon irradiation were

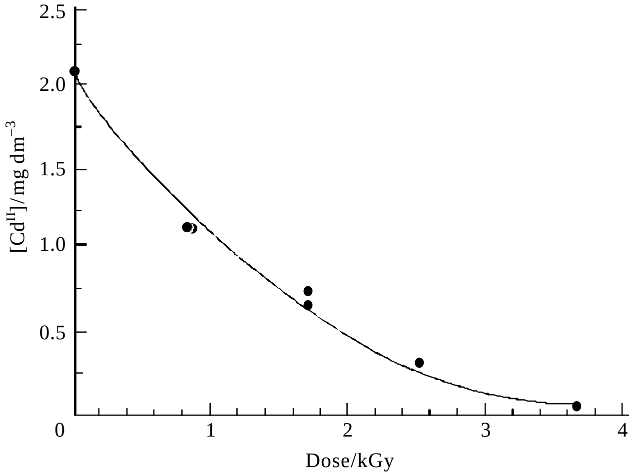

Figure 1 Dependence of Cd^{II} concentration in deaerated aqueous solution containing 5×10^{-3} mol dm^{-3} formate on the dose of electron radiation.

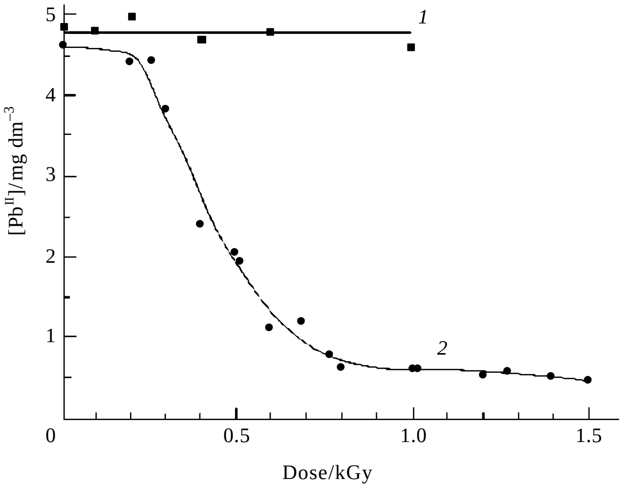

Figure 2 Dependence of Pb$^{\mathrm{II}}$ concentration in aerated aqueous solution in the absence of formate (*1*) and in the presence of 10^{-2} mol dm^{-3} formate (*2*) on the dose of electron radiation.

filtrated using glass filters or were centrifuged.

Figure 1 shows the dependence of the change in Cd$^{\mathrm{II}}$ concentration in the deaerated solution containing *ca.* 2 mg dm^{-3} Cd$^{\mathrm{II}}$ and 5×10^{-3} mol dm^{-3} formate on the dose of electron radiation. A dose of *ca.* 3.5 kGy leads to a decrease in Cd$^{\mathrm{II}}$ concentration below the permitted level of 0.1 mg dm^{-3}.[9] Note that irradiation of aerated solution at such a concentration of Cd$^{\mathrm{II}}$ did not give a positive result. At sufficiently high concentrations of Cd$^{\mathrm{II}}$ (for instance, at 50 mg dm^{-3}) the required removal level is reached even in aerated solutions. Under this condition reactions (1) and (2) can compete with the interaction of oxygen with e^-_{aq} and H.

Similar results were obtained with solutions of Pb$^{\mathrm{II}}$. The dependence of the decrease in Pb$^{\mathrm{II}}$ concentration in aerated solution containing *ca.* 5 mg dm^{-3} Pb$^{\mathrm{II}}$ in the absence of formate (curve *1*) and in the presence of 10^{-2} mol dm^{-3} formate (curve *2*) on the dose of electron irradiation is shown in Figure 2. In the absence of formate the removal of lead does not take place. The induction period is characteristic of the dependence expressed by curve *2*. Apparently, it is caused by the presence of oxygen in the solution, and is finished after oxygen consumption. The dose required to remove *ca.* 5 mg dm^{-3} Pb$^{\mathrm{II}}$ to the concentration less than 1 mg dm^{-3} (a permitted level of lead content[9] in disposed waste waters) is *ca.* 0.7 kGy. Slightly higher doses (1.0–1.2 kGy) are required for the removal of 10–20 mg dm^{-3} Pb$^{\mathrm{II}}$.

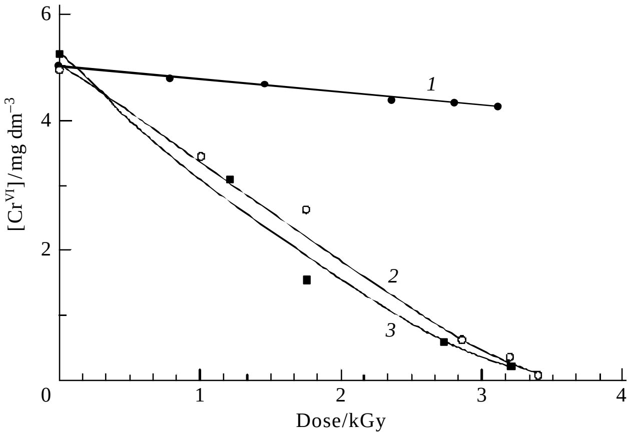

Figure 3 Dependence of Cr$^{\mathrm{VI}}$ concentration in aerated neutral aqueous solutions in the absence of formate (*1*) and in the presence of 9.6×10^{-3} mol dm^{-3} formate (*2*) and in deaerated neutral aqueous solution (*3*) in the absence of formate on the dose of electron radiation.

Chromate in aqueous solution is reduced to Cr$^{\mathrm{III}}$ upon electron-beam irradiation. The process occurs in deaerated and aerated solutions, in the absence and the presence of formate (see Figure 3). However, in aerated solutions in the absence of formate only 10–30% reduction occurs. Such a low degree of reduction seems to be caused by reactions (4)–(6); HO_2 and O_2^- radicals do not reduce Cr$^{\mathrm{VI}}$ ions in a neutral medium, but oxidize transient reduced species. In the presence of formate the process is very effective even in aerated solutions. Apparently, the $\mathrm{COO^{\cdot-}}$ radical ion formed in reaction (13) is a stronger reducing agent towards Cr$^{\mathrm{VI}}$ than HO_2 and O_2^- radicals. Note that the residual Cr$^{\mathrm{VI}}$ after a radiation dose of *ca.* 3.5 kGy is *ca.* 0.05 mg dm^{-3}. Chromium(III) is precipitated as the hydroxide. The medium for precipitation of Cr$^{\mathrm{III}}$ in this form is slightly-alkaline (pH 8.5–9.5, see *e.g.* ref. 10).

Hence, electron-beam treatment in combination with the use of formate as an hydroxyl scavenger and subsequent filtration or centrifugation can be used for the removal of cadmium, lead and chromium from water.

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