

Photocatalytic Degradation and Sorption of Radiocobalt from EDTA-Co Complexes
Using Manganese Oxide Materials - 12220

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ABSTRACT

The synthesised cryptomelane-type α - MnO_2 was tested for its Co-57 uptake properties in UV-photoreactor filled with 10 μM Co-EDTA solution with a background of 10 mM NaNO_3 . High cobalt uptake of 96% was observed after 1 hour of UV irradiation. As for comparison, a well-known TiO_2 (Degussa P25) was tested as reference material that showed about 92% cobalt uptake after six hours of irradiation in identical experiment conditions. It was also noted that the cobalt uptake on cryptomelane with out UV irradiation was modest, only about 10%. Decreasing the pH of the Co-EDTA solution had severe effects on the cobalt uptake mainly due to the rather high point of zero charge of the MnO_2 surface (p_{zpc} at pH ~ 4.5). Modifying the synthesis procedure we were able to produce a material that functioned well even in solution of pH 3 giving cobalt uptake of almost 99%.

INTRODUCTION

Nuclear power plants (NPP) produce large volumes of liquid radioactive waste. Solidification and volume reduction of these liquid wastes is required to decrease aquatic radioactivity emissions and to obtain suitable waste forms for final disposal. One widely used separation technique is ion exchange utilizing tradition organic ion exchangers or different inorganic ion exchangers. The advantage of inorganic ion exchangers over organic resins is their ability to resist decomposition at elevated temperatures and in ionizing radiation. Also the possibilities of safe storage and final disposal of the used materials have made these materials very interesting in nuclear waste management. Some of these inorganic materials such as zeolites, titanosilicates, sodium-titanates and hexacyanoferrates have already made their way to commercial application, mainly for the separation of fission nuclides Cs-137 and Sr-90, replacing older technologies based on evaporation and organic ion exchange resins [1,2].

Nevertheless inorganic ion exchangers have some serious disadvantages. The operating pH-range is usually rather narrow due to the low acidic nature of the exchange material (typical $pK_a \sim 4$), thereby limiting ion exchange use. Furthermore, the chemical stability of inorganic materials can be problematic, for example, dissolution of aluminium from zeolites at pH extremes.

Liquid wastes from NPPs contain high amounts of inactive metal ions such as K^+ , Na^+ and Ca^{2+} and quite often only trace concentrations of radionuclides. Thus a high selectivity is required to efficiently remove the radionuclides and to obtain a minimal amount of waste (i.e. spent sorbent) for final disposal. Due to its relatively long half-life (5.2 a) and high gamma decay energy, Co-60 is one of the most problematic waste nuclides in NPP liquid waste streams. Many of these waste streams contain complexing agents such as EDTA and oxalate originating from cleaning and decontamination solutions used in NPPs. Removing Co from its EDTA complexes is difficult due to their high stability constants. Cation exchange resins have normally been used for the removal of Co-60, and in addition recent studies have proven the efficiency of highly selective inorganic ion exchangers for its removal [3, 4]. However, as soon as Co-60 is complexed, for example with EDTA, both methods turn out to be quite inefficient.

Four-valent metal oxides are known to have interesting ion exchange properties [5]. Some of these metal oxides have semi conductive properties and for example TiO_2 – UV systems have been tested widely and used in several applications for degradation of organic molecules and substances. The theory behind this is that when TiO_2 is irradiated by UV radiation at wavelengths of 390 nm or less, it produces electron-hole pairs. The holes are located in the TiO_2 valence band and they can migrate to the catalyst surface and oxidize organic compounds. In addition, the conduction band electrons produced by the irradiation of TiO_2 can reduce oxygen in solution to superoxide, forming additional hydroxyl radicals with a strong oxidation potential [6,7]. The combination of ion exchange properties and oxidation potential makes these metal oxides very interesting for their possible use in nuclear industry. In addition to TiO_2 also manganese oxides have shown interesting oxidation potential and ion exchange properties. α - MnO_2 is well-known for its extreme selectivity for Ra and good transition metals uptake properties. Manganese oxides are a family of well over 20 members with different Mn/O ratios and structures from which we chose two different structures: layered birnessite-type and tunnel structured cryptomelane-type oxides [10]. From ion exchange point of view the birnessite-type manganese oxide should have higher capacity while the cryptomelane-type should be more selective due to its tunneled structure [11]. Our idea was to simultaneously test the oxidation potential and the ion exchange properties of these manganese oxides in fluidized bed –type UV-reactor.

METHODS

Analytical grade $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Riedelde Haen) and $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ (Merck) were used without further purification. Test solutions were prepared by dissolving $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (10 μM) and $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ (10 μM if not otherwise stated) in Milli-Q water (18M Ω /cm). The solutions were traced with Co-57 (Eckert & Ziegler Isotope products). Also background ions of NaNO_3 (10 mM if not otherwise stated) were added to the solution in order to have more realistic experiment conditions. The Co speciation of the test solutions was calculated using Visual MINTEQ program Table 1 [12]. UV irradiation was carried out in 100 ml immersion well reactor (Photochemical Reactors Ltd., Model 3312), equipped with a 6 W low-pressure mercury lamp (254 nm), using 80 ml of solution and appropriate mass of metal oxide (0.8 g for BF 100 and 0.16 g for BF 500). Temperature was controlled by a thermostat TTM-000 Series (TOHO Electronics Inc., Japan) during irradiation.

In all experiments, the metal oxide powders were separated from the solution by centrifugation (Sepatech Megafuge 1.0, Heraeus) for 10 minutes at 4,000 rpm (3,000 G). The solution was filtered with a 0.2 mm Acrodisc filter (PALL Life Sciences) and pH was measured with an Orion 3 star pH meter. The filtered aliquots (5 ml) of the solution were counted for Co-57 with an automatic gamma counter (Wallac 1480 Wizard 3). The removal percentage value for Co-57 sorption was calculated using Equation (1):

$$\text{Removal \% of Co - 57} = \frac{A_0 - A}{A_0} \times 100\% \quad (\text{Eq. 1})$$

where A_0 is the initial Co-57 activity of the test solution and A is the Co-57 activity of the solution after the solid phase separation. Also distribution coefficients (K_d) were used to compare Co uptake when different batch factors were used in the experiments. The K_d values were calculated using Equation (2):

$$K_d = \frac{(A_0 - A)}{A} \times \frac{V}{m} \quad (\text{Eq. 2})$$

where V/m is the solution volume to sorbent mass ratio (batch factor, BF in ml/g).

Table 1. Speciation of Co in solution composed of 10 μM $\text{Co}(\text{NO}_3)_2$, 10 μM Na_2EDTA , 10 mM NaNO_3 solution at pH 3 and 6.

Solution pH 3		Solution pH 6	
10.3 %	Co^{+2}	0.02 %	Co^{+2}
0.1 %	CoNO_3^+	99.78 %	CoEDTA^{-2}
28.9 %	CoEDTA^{-2}	0.2 %	CoHEDTA^-
56.7 %	CoHEDTA^-		
4.0 %	$\text{CoH}_2\text{EDTA}(\text{aq})$		

RESULTS

The cation exchanger nature of the tested metal oxides and the formation of negatively charged Co - EDTA complexes resulted in poor Co-uptake from 10 μ M Co – EDTA solution with a background of 10 mM NaNO₃ at pH 6 with both of the manganese oxides Figure 1. However, the effect of UV-radiation was rapid and significant (>65%) Co uptake was observed already after 15 and 60 min with cryptomelane- and birnessite-type manganese oxides, respectively. The well-known Degussa P25 TiO₂, taken as reference material to the experiments, showed the slowest Co uptake profile. As high as 97.5% Co uptake was observed with cryptomelane-type manganese oxide while birnessite-type achieved 92% uptake after 4 hours of UV irradiation. Also, 92% Co uptake was achieved with TiO₂ but only after six hours of irradiation. Due to the relative fast kinetics and high Co uptake, the cryptomelane-type manganese oxide was chosen for the following experiments.

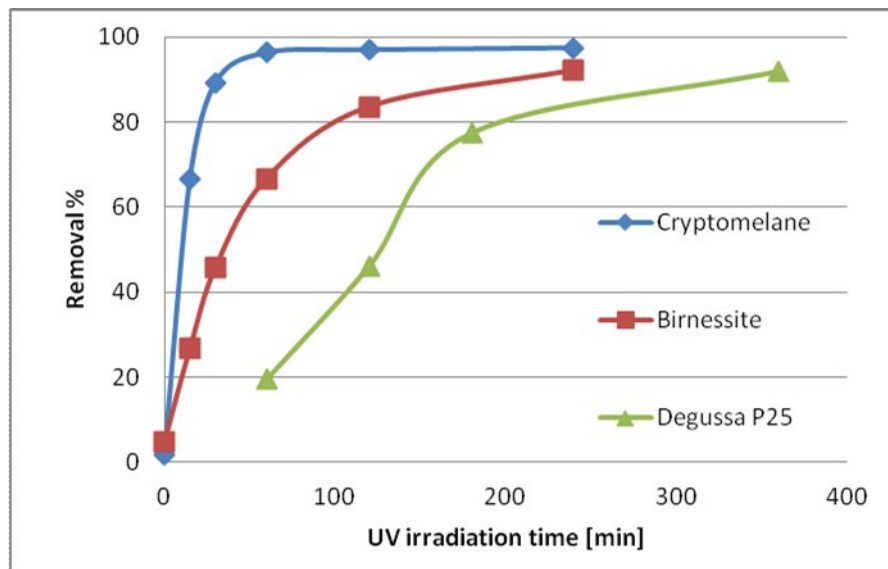


Figure 1. The Co removal percentage as a function of UV irradiation time (min), solution pH 6.

Effect of pH

Considering the rather high point of zero charge (pzc) values of the tested metal oxides, pH 4.5 and 4.7 for MnO₂ and TiO₂, respectively [13], and typically the slightly acidic waste solutions of nuclear industry the UV-experiments were repeated in lower pH

Figure 1 (pH ~3). At pH 3 the Co uptake trend of TiO₂ was decreasing as a function of UV-irradiation time from initial ~20% to <1% sorption. Cryptomelane, however, showed a similar Co uptake trend as it did at higher pH but the uptake level was considerable lower. Even though the maximum Co uptake of cryptomelane was near 75% at pH 3 it was not enough considering the high decontamination demands of nuclear industry. The manganese oxide synthesis was modified in order to enhance the materials cation uptake properties in solution of lower pH. The modified manganese oxide (MoMO) showed excellent Co uptake resulting over 96% Co removal level after 60 min of UV irradiation and reaching over 98% Co removal after four hours Figure 2.

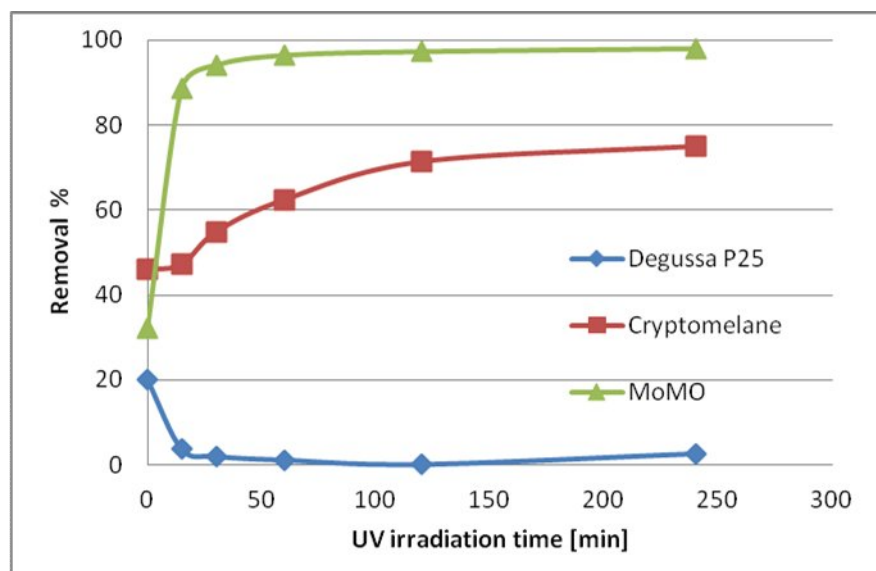


Figure 2. The Co removal percentage as function of UV irradiation time (min), solution pH 3.

Selectivity and capacity

A simple selectivity test for the MoMO material was done by changing the ionic competition of the solution matrix. The background ion, Na⁺ and NO₃⁻, concentration was varied from 1 mM to 100 mM in order to have clear difference in the competition of ion exchange sites of the material Figure 3. The Co-EDTA concentration was kept in 10 μM. The increase in competing ions didn't have significant effect on Co uptake demonstrating the materials high selectivity towards Co ions.

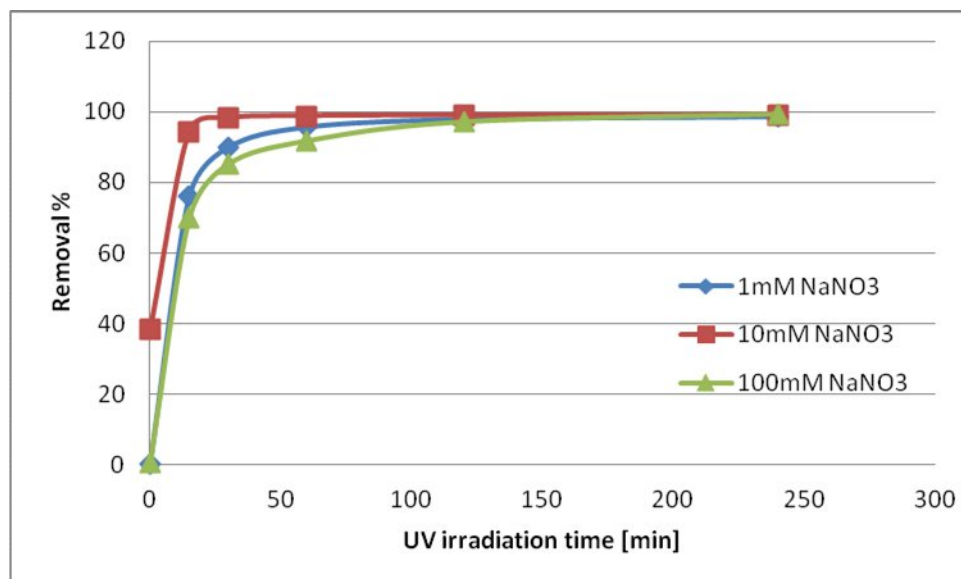


Figure 3. The Co removal percentage of modified manganese oxide (MoMO) as function of UV irradiation time (min), solutions pH 6.

The capacity of the MoMO material was tested by increasing the batch factor (BF) of the UV experiment from BF 100 to 500 i.e. decreasing the mass of the oxide Figure 4. The solutions used here were $1\mu\text{M}$ and $10\mu\text{M}$ Co-EDTA solutions at pH 6. The increase of BF had clear effect on the Co uptake and the plotted distribution coefficient (K_d) curves visualized the effect of change in the EDTA/metal oxide ratio on the Co uptake in a logical order.

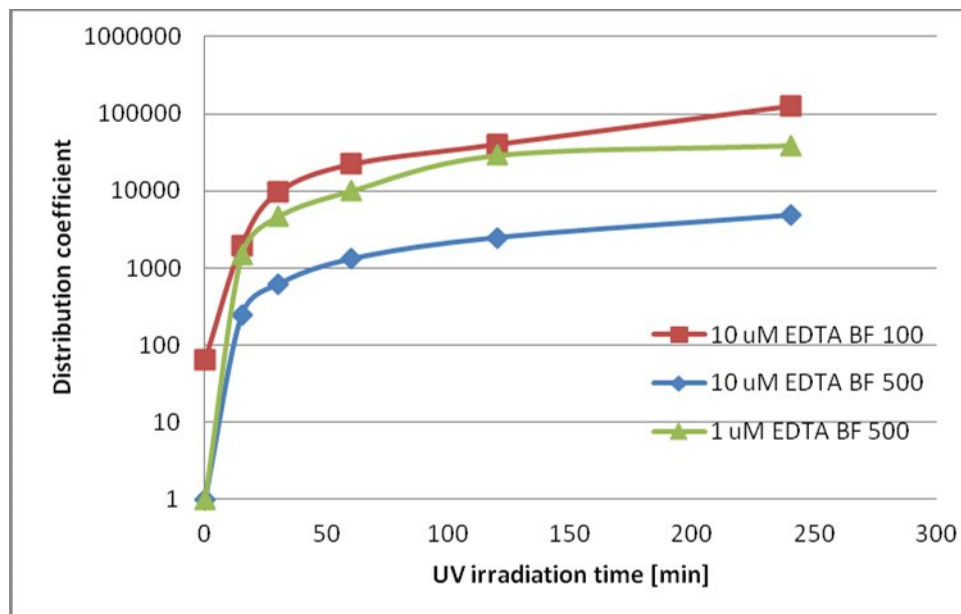


Figure 4. The distribution coefficients (K_d , ml/g) of Co as function of UV irradiation time (min) using modified manganese oxide (MoMO), solutions pH 6.

CONCLUSIONS

The known properties, catalytic and ion exchange, of manganese oxides were simultaneously used for the separation of EDTA complexed Co-57. Tunnel structured cryptomelane –type showed very fast and efficient Co uptake properties outperforming the well known and widely used Degussa P25 TiO₂ in both counts. The layered structured manganese oxide, birnessite, reached also as high Co removal level as the reference material Degussa did but the reaction rate was considerably faster. Since the decontamination solutions are typically slightly acidic and the point of zero charge of the manganese oxides are rather high > pH 4.5 the material had to be modified. This modified material had tolerance to acidic solutions and it's Co uptake performance remained high in the solutions of lower pH (pH 3). Increasing the ion concentration of test solutions, background concentration, didn't affect the final Co uptake level; however, some changes in the uptake kinetics could be seen. The increase in EDTA/MoMO ratio was clearly reflected in the Co uptake curves.

The obtained results of manganese oxide were very promising for the treatment of EDTA complexed Co solutions. The better performance values and cheaper production cost of manganese oxide, compared to titanium dioxide, is so big driving force that further studies on the material are evident. The possibilities for continuous treatment, instead of the fluidized bed –type batch experiment are investigated and the effects of other compounds affecting the decomplexation of Co-EDTA are further studied.

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