Study of the Effects of Electron Beam on Heavy Metals in Presence of Scavengers for Decontamination and Purification of the Municipal and Industrial Wastewater

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Abstract. Radiation processing technology has been proven to purify and decontaminate the textile industrial wastewater. The research work undertaken that has overall goal to better understand the EB processing of wastewater containing heavy metals. This research have conducted our study to examine the effects of Electron Beam on laboratory made samples and real samples with complex matrix heavy metals such as Pb and Cd in the presence or absence of rice bran as metal scavenger. A MeV Rhodotron accelerator system of Yazd Radiation Processing Center with the beam power of 100 Kw was used for irradiation. The concentration of metal ions in the samples before and after irradiation was measured by graphite furnace atomic absorption spectrometry. Samples of Lead and Cadmium in distilled water or in solution containing either Sodium acetate (0.001 M) or Ethylene diamine tetra- acetate (0.001 M) were prepared. It was found that, the capability of rice bran for sorption of metal ions in the presence of sodium acetate (Na CH_3COO) and ethylene diamine tetra-acetate (EDTA) is lowered. Then, the effect of electron beam irradiation with different doses of 1, 3, 6, and 9 kGy on the laboratory made samples, the wastewater samples taken from the Yazd municipal wastewater plant and textile industry was considered. Results showed that in the presence of rice bran as scavenger the concentration of metal ions in solutions containing either chemical reagent of Na CH_3COO or EDTA, after irradiated by electron beam has significantly decreased.

1. ntroduction

The pollution of natural water by both biological and chemical contaminations is worldwide problem, few populated areas do not suffer from one form of water pollution or another [1]. In recent years the pollution of water and wastewater by heavy metals has received considerable attention. Apart from aerosols in the atmosphere and direct effluent discharges into waters, the concentration of heavy metals available to aquatic system is determined by the solubleization and release of metals from rock-forming minerals, adsorption and precipitation reaction which occur in soils and sediments, or industrial activities and waste disposal. The solubility of metal ions in solution will depend on the concentration of anions and chelating ligands present in water, its pH and redox status, and the presence of adsorbent sediments.

Wastewater treatment plants produce great amounts of sludge, which can be dried and used as landfill or fertilizer. It is very important to know the concentration of heavy metals in sludge and wastewaters discharged to the interceptors. The concentration of heavy metals in sludge used for composting has to be very low.

Radiolytic removal of heavy metals from the wastewater using electron beam radiation has been reported [3,4]. The method is based on radiation-chemical reaction of the metal ions to their respective metals or lower oxidation state ion in the absence of oxygen in the water. It is also necessary to use a scavenger to remove the OH radicals formed in the water during radiation treatment. We recently reported that electron beam irradiation is capable of conversion of organometalic compound (methyl) mercury into inorganic mercury ion [5]. It is also known that synthetic and natural sorbant have capability of elimination of metal ions from water samples [6,7], however, when metal ions are presented in the complex form or as organometalic compound the uptake of sorbent is reduced. Therefore in this study the capability of rice bran, a natural byproduct for sorption of metal ions in the presence of organic reagents such as ethylene diamine tetra acetic (EDTA) and sodium acetate (CH_3COONa), before and after irradiation with electron beam was considered. Furthermore, the study was extended for removal of metal ions from wastewater samples.

2- Mechanism of radiolytic conversions of metal ions using electron beam irradiation suggested by Pikaev [4]

One of the suggested mechanisms for radiolytic metal removal is based on the radiation-chemical reduction of metal ions to their corresponding metals or to lower oxidation state ions, followed by its removal with filtration. The reduction is the results of reaction of pollutants with reducing products of water radiolysis (e_{aq} and H atoms) and short-lived species from added solutes.

In case of Cd(II) ions the mechanism can be written as:

$$Cd(II) + e_{aq} \rightarrow Cd(I) \tag{1}$$
$$Cd(II) + H \rightarrow Cd(I) \tag{2}$$
$$Cd(I) + Cd(I) \rightarrow Cd(0) + Cd(II) \tag{3}$$
$$nCd(0) \rightarrow Cd(0)_n \tag{4}$$

However, Cd(I) ions participate not only in reaction 3, but also, are oxidized by OH radicals and hydrogen peroxide(the water radiolysis products) and HO_2 formed in reactions of e_{aq} and H atoms with oxygen present in the system:

$$Cd(I) + OH \rightarrow Cd(II) + OH^- \tag{5}$$
$$Cd(I) + H_2O_2 \rightarrow Cd(II) + OH + OH^- \tag{6}$$
$$Cd(I) + HO_2 + H^+ \rightarrow Cd(II) + H_2O_2 \tag{7}$$

So, the net result is no radiation-induced reduction of heavy metal ions. To suppress the reaction 5-7, two requirements are necessary; the absence of oxygen in the water and the presence of a scavenger of OH radicals. In the presence of format ions, OH radicals (and H atoms) are converted to COO^- radical ions which reduce Cd(II) and Cd(I) ions:

$$HCOO^- + OH(H) \rightarrow COO^- + H_2O(H_2) \tag{8}$$
$$Cd(II) + COO^- \rightarrow Cd(I) + CO_2 \tag{9}$$
$$Cd(I) + COO^- \rightarrow Cd(0) + CO_2 \tag{10}$$

Causing reduction of Cd(II) to Cd Cd(0). In principle, the same mechanism is valid for water containing Pb(II) ions.

If Cd(II) and Pb(II) ions are simultaneously present in water, Cd(II) reduction is observed after reduction of a considerable part of Pb(II) ions[3]. Hence, ionizing radiation such as electron beam can be used for radiolysis removal and pre-concentration of heavy metals from water and wastewaters. However, another approach is the removal of the sample metal ions produced by electron beam irradiation with a natural scavenger such as rice bran.

3. Experimental

3-1. Sample preparation

Laboratory-made water samples and also wastewaters samples produced during the Yazd wastewater treatment plant were analyzed. The wastewaters samples were: input mixed wastewater, and outlet wastewater. 40 ml of each sample were irradiated in Petri dishes. $NaCH_3COO$ and ethylene diamine tetra acetic (EDTA) were added to the samples as complexing agent. Rice bran was used as natural sorbent. The rice bran was washed with sulfuric acid before use [6].

3.2. Electron beam irradiation system

Samples were irradiated by 10 MeV electron beam of RHODOTRON TT200 accelerator of the Yazd Radiation Processing. The specifications of the electron beam accelerator are given in Table 1. Irradiation doses were 1, 3, 6 and 9 kGy.

TABLE I. RHODOTRON TT200 ELECTRON BEAM ACCELERATOR PARAMETERS.

Beam Energy	5 and 10 MeV
Beam power at 10 MeV	70 kW
Beam power at 5 MeV	35 kW
Energy dispersion at 10 MeV	±300 keV
Scanning range	30-100 cm
Total power consumption	≤ 300 kW
RF	107.5 MHz
RF power output	200 kW
Electron gun average current	0-10 mA
Resolution	±50 µA

FIG 1. Rice bran was added into the sample.

3.3. Determination of metal ions

A furnace atomic absorption spectrometer with Zeemens background correction was used for determination of metal ions in un-irradiated and irradiated samples.

4. Results

The concentration of metals in laboratory-made water samples containing lead and cadmium and irradiated with electron beam were measured and are presented in Table 2. Different amount of 4, 8, and 12 mg of natural scavenger were used throughout the study. The samples were irradiated by EB accelerator system at doses of 1, 3, 6 and 9 kGy as shown in the Table 2. The effect of irradiation on samples containing EDTA and Sodium acetate as scavenger was also studied and the results are demonstrated in table 3 and 4. The data obtained from irradiation of different samples from municipal wastewater with added scavengers are presented in Table 5. Wastewater samples containing Cd and Pb and either Sodium acetate (CH_3OONAa) or EDTA chemical reagent and natural scavenger were irradiated and results are given in table 6.

TABLE II. CONCENTRATION OF Cd and Pb IN LABORATORY-MADE WATER SAMPLE (100 PPB) AFTER IRRADIATION BY ELECTRON BEAM IN PRESENCE OF NATURAL SCAVENGER.

Cd (ppb)	Pb (ppb)	Scavenger (mg)	Absorbrd Dose (kGy)
100	100	-	0
86.8±1.7%	94.2±0.5%	-	1
95.8±6%	79.3±6.3%	-	3
95.7±1.8%	95.1±7.8%	-	6
94.3±4.3%	93.0±5.4%	-	9
87.8±2.6%	59.1±4.8%	4	1
79.1±2.3%	67.0±5.1%	4	3
81.8±5.8%	69.5±3.5%	4	6
83.7±4%	52.5±4.9%	4	9
79.8±6.1%	51.5±0.3%	8	9
82.2±5.6%	34.3±8.9%	12	9

TABLE III. IRRADIATION OF LABORATORY-MADE WATER SAMPLES CONTAINING Cd AND Pb and EDTA,(0.001 MOLAR) WITH AND WITHOUT SCAVENGER.

Cd (ppb)	Pb (ppb)	Scavenger (mg)	Absorbed Dose (kGy)
100	**100**	----	0
48.3 ± 5.3%	34.0 ± 1.7%	12	1
47.3 ± 3.8%	31.9 ± 7.6%	12	3
38.1 ± 6.3%	25.4 ± 0.2%	12	6
47.6 ± 2.6%	27.0 ± 10%	12	9

TABLE IV. IRRADIATION OF LABORATORY MADE WATER SAMPLES CONTAINING Cd, Pb AND SODIUM ACETATE ($NaCH_3OO$, 0.001 MOLAR) WITH AND WITHOUT SCAVENGER.

Cd (ppb)	Pb (ppb)	Scvenger (mg)	Absorbed Dose kGy
100	100	0	0
10.1 ± 0.4%	7.3 ± 0.8%	12	1
5.9 ± 2.9%	2.6 ± 5.5%	12	3
6.4 ± 0.1%	1.1 ± 12.2%	12	6
5.4 ± 0.5%	0.8 ± 15.1%	12	9

TABLE V. Cd CONCENTRATION IN UN-IRRADIATED AND IRRADIATED MUNICIPAL WASTEWATER WITHOUT SCAVENGER.

Cadmium (Cd)	Absorbed Dose (kGy)	Municipal Wastewater
4.2±9.7%	0	Mixed wastewater (inlet)
0.5±1.2%	1	"
1.1±1.7%	3	"
4.9±12.4%	6	"
1.3±29%	0	Wastewater (outlet)
1.2±1.1%	1	"
0.5±11%	3	"
2.1±5.8%	6	"
0.7±4.1%	0	Wastewater (inlet)
2.2±11.7%	1	"
0.6±16.5%	3	"
0.4±32.6%	6	"

TABLE VI. IRRADIATION OF WASTEWATER SAMPLES CONTAINING Cd AND Pb, SODIUM ACETATE ($NaCH_3OO$) OR EDTA CHEMICAL REAGENT INCLUDING NATURAL SCAVENGER.

Cd (ppb)	Pb (ppb)	$NaCH_3COO$ Or EDTA	(Scavenger) (mg)	Irrradiation Dose (kGy)
0.6	2.8±2.2%	–	––	0
0.1±18.9%	N.D.[1]	$NaCH_3COO$	12	1
0.1±8.7%	N.D.	$NaCH_3COO$	12	3
––––––	N.D.	$NaCH_3COO$	12	6
0.2±0.3%	N.D.	EDTA	12	1
0.2±3.6%	N.D.	EDTA	12	3
0.2±44.3%	N.D.	EDTA	12	6

[1] Not detected

5. Conclusion

From the above studies the following conclusion can be drawn:
Radiation purification of polluted water and wastewater depends on the nature and concentration of the metals and chemicals in the samples.
Electron beam irradiation of water and wastewater samples containing heavy metals such as lead and cadmium can increase the concentration of free ions in the samples. Addition of natural scavenger together with EB radiation can increase the heavy metal removal from the wastewater samples. Under the same conditions the removal of lead ion was more significant.
Results of EB irradiation of the water and wastewater samples containing heavy metals and natural scavenger in the presence and absence of EDTA and $NaCH_3COO$ show that the capability of the natural scavenger in the presence of chemical agents is increased. Moreover, the efficiency of the scavenger for removal of the lead ion is more significant.

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