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Bioaccumulation of ^{137}Cs and ^{60}Co from radioactive waste streams using *Veronica anagallis-aquatica*

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ABSTRACT

Efficiency of *Veronica anagallis-aquatica* plants for bioaccumulation/biostabilization of ^{137}Cs and ^{60}Co from radwaste solution simulates was evaluated on batchwise laboratory scale experiments. The plants were added to the spiked solutions having four different initial activity concentrations of ^{137}Cs and ^{60}Co. Additional factors such pH values, the amount of biomass and the light exposure that assumed to affect the treatment process were studied systematically. The uptake values of ^{137}Cs from the simulated waste solution were inversely proportional to the initial activity contents and directly proportional to increase in the plant mass and sunlight exposure. Bioaccumulation of ^{60}Co is independent on its initial activity concentrations. The spiked solution of pH $\approx$ 4.9 was found to be the suitable medium for the treatment process. The present study suggests that *Veronica anagallis-aquatica* could be used as a potential candidate plant for phytoremediation for the radioactive wastes especially those contaminated with radiocesium and/or radiocobalt.

INTRODUCTION

It is becoming increasingly difficult to ignore the developed applications of living systems in hazardous materials remediation. Phytoremediation is a technology with tremendous possibilities; it has applications for remediation of groundwater, industrial effluents, radioactive waste, and landfills. Phytoremediation is aesthetically pleasing where it is perceived as a more natural solution than the conventional treatment methods. The cost and maintenance are little compared to that of the others. Although this technology is relatively new, it is progressing, quickly developed and may become the promising method for remediation technologies.

Radionuclides enter the soil and water through different human activities such as mining and milling of nuclear fuel, operations typical of nuclear fuel cycle, full out from nuclear weapon testing and occasional nuclear disasters such as those in Chernobyl in 1986 and Fukushima in 2011 poses serious problems to biological systems[1-3].

Radioisotopes of ^{37}Cs with a half-life of 30.0 years and ^{60}Co of half-life 5.25 years constituted part of the main artificial radionuclides produced by nuclear fission. It is being introduced into the terrestrial environments by nuclear applications, authorized discharge of nuclear waste and nuclear accidents such as the Chernobyl accident in 1986 and Fukushima in 2011[4]. As a consequence, it is necessary to eliminate these radionuclides from contaminated solutions to reduce the hazardous effects to humans. Potential of plants to remove radionuclides and/or toxic elements from soils and solutions can be also successfully applied for the removal of many hazardous ra-

Figure 1: ***Veronica anagallis-aquatica*** **(L.) present in El-Manayf Canal, Ismailia**

dionuclides such as ^{137}Cs and ^{60}Co.

Phytoremediation, the use of green plants for remediation of soil and solutions contaminated with low level of toxic metals and radionuclides has received a lot of attention in the last few years due to its environment-friendly nature and aesthetically pleasing qualities[5,6]. Many studies have been conducted to determine the efficiency of aquatic plants in accumulation of heavy metals and radionuclides.

In the present communication, the capability of *Veronica anagallis-aquatica* plant known as Water Speedwell, for bioaccumulation for ^{60}Co and ^{137}Cs was investigated by growing the plant into solutions spiked with the radiocesium and radiocobalt. The results of present study will discuss the capability of *Veronica anagaliss-aquatica* to uptake the two radionucliuades, either alone or in combination. The process was performed under different experimental conditions such as, different pH values of the waste solution, varied initial activity contents, biomasses of the tested plant used and the sunlight effect.

EXPERIMENTALAPPROACH

Processing of biomass

Fresh green plant *Veronica anagallis-aquatica (L.)* was obtained from El-Manayf Canal (a branch from the Nile River, Ismailia), Figure 1. The proposed plant was identified at the herbarium of the National Research Center, Egypt. The tested plants were washed with tap water and kept in sunny place with a gradual addition of tap water versus the self-environmental water for nearly one week before starting the experimental work.

Five grams replicates of the batch *Veronica anagallis-aquatica* fresh healthy plants were separated, washed by tap water and immersed in jars containing 50ml tap water spiked with ^{60}Co and ^{137}Cs individually or as a mixture.

The plant was allowed to grow under various experimental conditions such as: contact time (up to 100 hours), sunlight, various amounts of the biomass (5-15 grams), increasing initial radioactivity contents of the waste solution (30-260 Bq/ml) and the pH values of the solution under treatment (2.9-10.9). The phytoremediation process was followed by counting the activities remained in the treated streams, and the data reached were discussed precisely.

Radionuclides for spiking waste solution

The radionuclides used in the present study were ^{137}Cs as CsCl of radioactive concentration 127MBq/ml and purity more than 99.5% and ^{60}Co as $CoCl_2$ of radioactive concentration 115MBq/ml and purity more than 99% purchased from Institute of Atomic Energy, POLATOM, Poland. The aqueous radioactive waste solution was simulated by spiking tap water with predetermining amounts of the two radioisotopes. The chemical analysis of water used is shown in the TABLE 1.

Solutions with increasing initial activity contents and various pH values were prepared and subjected to treatment process using *Veronica anagallis-aquatica (L.)*. Dilute HNO_3 or dilute NaOH solutions were used to adjust the predetermined pH values. The initial ra-

TABLE 1: Concentrations of some ions of interest in used tap water

pH	Soluble cations (ppm)				Soluble anions (ppm)		
	K^+	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
6.90	0.086	1.07	1.2	1.4	0.77	0.7	1.8

ppm = mg/1

dioactivity contents and at different content intervals in the test solutions were measured using multichannel analyzer, PCAP, USA.

Data evaluation

The obtained data were assessed based on the following relations:

$$\text{Uptake \%} = \frac{\text{initial activity in waste solution} - \text{remaining activity in waste solution}}{\text{initial activity in waste solution}} \times 100$$

Concentration ratios (CR) and transport indices (TI) were calculated for the dry matter as the ratio of the radioactivity in the living plant (Bq/kg dry wt.) to the radioactivity in the water (Bq/l)[7,8].

$$CR = \frac{\text{radionuclide content in the dry plant, Bq/g}}{\text{radionuclide content in the waste solution, Bq/ml}}$$

$$TI = \frac{\text{radionuclide content of the shoot, Bq/g}}{\text{radionuclide content of the whole plant, Bq/g}} \times 100$$

RESULTS AND DISCUSSIONS

Bioaccumulation of ^{137}Cs and ^{60}Co at various activity contents

Veronica anagallis-aquatica as one of aquatic plants seems to have high capability to accumulate radionuclides. It could be claimed that this plant still not completely discussed as phytoremediation agent, where it was investigated by few literatures, concerning with the experimental observations for bioabsorption of ^{137}Cs and ^{60}Co by using *Veronica anagallis*, it was clearly investigated that the maximum accumulation percentage was reached after the first 24 h from the starting time of the treatment process.

In this study, the effect of initial activity concentrations of ^{137}Cs and ^{60}Co mixed in aqueous solution was studied as a function of biosorption efficiency studied in the range of different activities (31Bq/ml – 105Bq/ml), (32Bq/ml – 93Bq/ml) for ^{60}Co and ^{137}Cs, respectively. Figure 2, shows that the removal of ^{137}Cs is inversely proportional to its initial activity contents. Increasing the initial content of ^{137}Cs accompanied by gradual increasing in the uptake percentage and continuing increase in the initial ^{137}Cs contents added results in drop of uptake percent. On the other hand, different concentrations of ^{60}Co have nearly the same high removal rate percentages. The back release of radiocobalt started directly in the relatively highest initial activity concentration (≈105 Bq/ml for ^{60}Co and 93 Bq/ml for ^{137}Cs) after the second day of treatment. Consequently, the increase in radioactivity contents of ^{137}Cs could diminish the accumulation rate according to the radiotoxic effect of ^{137}Cs as reported in literature[8].

Conversely, the removal of ^{60}Co during the first 24h at various activity concentrations is high and reached more than 95% of the removal percent. This behavior could be attributed to the vital role of Co in the growth of numerous plants including the aquatics[9,10]. Therefore, it could be concluded that the removal percentages of ^{60}Co by *Veronica anagallis* were mostly not affected by increasing the initial radioactivity contents in the simulated waste solution. On the contrary, the bioaccumulation of ^{137}Cs was decreased by increasing the initial activity contents in the spiked waste streams. The main radiotoxicty symptoms such that stunted

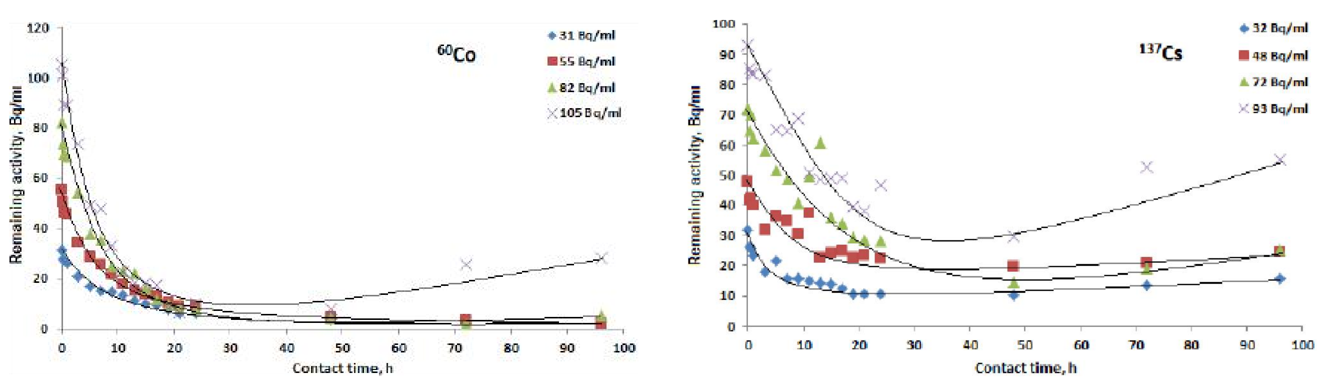

Figure 2: The effect of initial radioactivity contents on the removal efficiency of *Veronica anagallis* for ^{60}Co and ^{137}Cs.

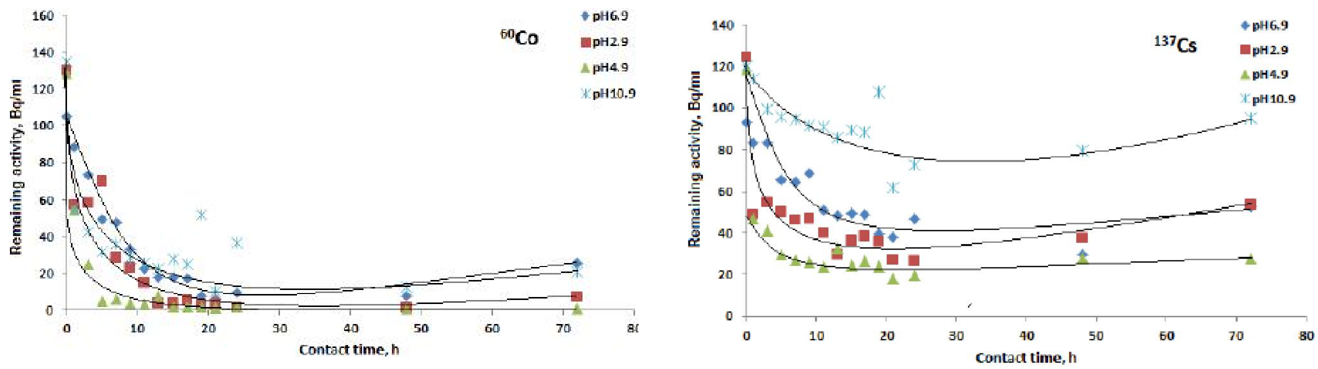

Figure 3: Bioaccumulation of ^{60}Co and ^{137}Cs at various pH media

growth, chlorosis of leaves with reddish brown spots that can be followed by necrosis of the plant tissue were observed following the exposure. Therefore, simultaneous substantial active effluxing possibly through the plant tissue and by time leaching of radioactivity from the necrosed tissue could be the key mechanism as the activity content in the simulated aqueous waste drastically increased after the first 24 hours. This behavior is in agreement with the previous literature[11].

Based on the results reached it could be stated that, the optimum time for the treatment process is near 24 h and after that time the plant should be removed from the media and treated as solid waste and fresh batch of plant can be added to continue the phytoremediation process.

Effect of changing pH on the efficiency of biaccumulation rate

Unpolluted fresh water streams, in balance with atmospheric carbon dioxide are having a pH of 5.6. Almost everywhere in the world the pH of rain is lower than this value. The main pollutants responsible for acid deposition (or acid rain) are sulfur dioxide (SO_2) and nitrogen oxides (NO_x). Acid deposition influences mainly the pH of freshwater. Much of the damage to aquatic life in sensitive areas with this little buffering capacity is a result of 'acid shock'. To imitate the natural environment of contaminated streams at different pH, diluted solutions of HNO_3 and NaOH were prepared and used to adjust the pH of the tested aqueous solutions. Figure 3 shows the variation of ^{60}Co and ^{137}Cs bioaccumulation in solutions with various pH values. The results showed decreases of ^{60}Co and ^{137}Cs in the solutions during the treatment period but in different rates according to the pH values 4.9, 2.9, 6.9 and 10.9 respectively. A rapid decrease was observed during the first five hours then slight decline going towards a relatively constant value was detected. It is apparent that as pH increased.

However, at low pH value of 2.9, there is high concentrations of H^+ in solution close to the cell surface which lead to greater competition between the H^+ at one side and Co^{2+} and/or Cs^+ ions at the other competing binding sites at the cell surface[12-14]. Thus the uptake of ^{60}Co and ^{137}Cs was decreased. On the other hand, at higher pH, Co^{2+} could react with OH^- and precipitate as hydroxides from the solution, leading to very low availability to the plant[15]. It could be concluded that the optimum pH value of aqueous solution is 4.9 while increasing or decreasing in pH of the waste solution appeared to affect the behavior of bioaccumulation of *Veronica anagallis-aquatica (L.)* to ^{60}Co and/or ^{137}Cs.

Changing the biosorption rate as a factor of biomass added

Figure 4 shows that there is a relationship between ^{137}Cs uptake abundance in the target plant and the various biomass amounts used while, slight increase in ^{60}Co uptake is accompanying with the increase in biomass. Generally, the amount of biomass added to the waste solution of fixed volumes seems to influence the uptake of the radiocontaminants. Decrease in the biouptake values by adding more biomass amounts may be explained on the basis that aquatic plants form a dense mat over the waste solution implies its ability to clear wide area and for fast bioaccumulation of the radiocontaminants. These results are in agreement with the previously published work by El-Gendy et al.[16].

Clearly the increase in the added biomass enhances positively the efficiency of the aquatic plant, *Veronica anagallis-aquatica (L.)*, to accumulate the radionuclides from simulated waste streams and forms a dense mat cover the solution surface implies its ability to survey up a

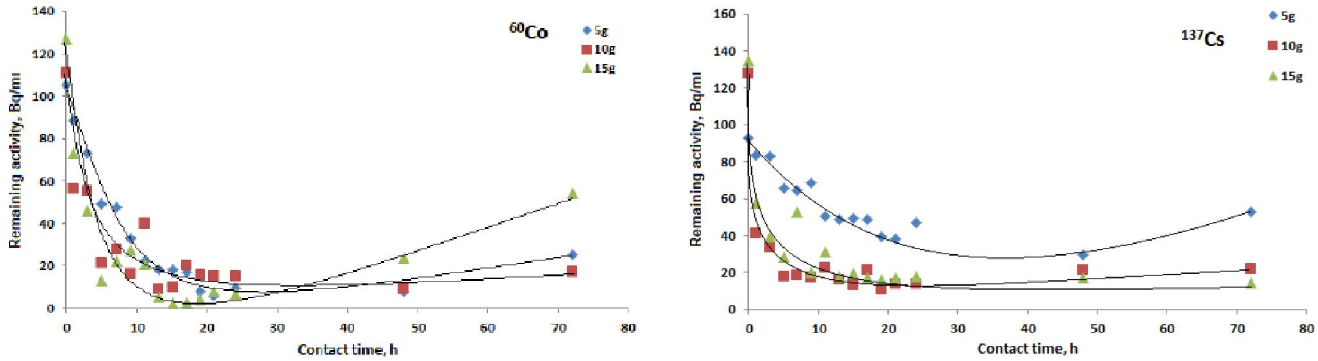

Figure 4: The effect of added biomass amounts on the biouptake of Veronica for ^{137}Cs and ^{60}Co.

wide area for quick removal of the radionuclides.

The effect of radionuclides species found individually or mixed in waste solution on the bioaccumulation efficiency

Bioremoval of ^{60}Co and/or ^{137}Cs by *Veronica anagallis-aquatica (L.)* from the aqueous waste solution containing these two radioisotopes either individually or as on a mixture was studied. Figure 5 shows that the removal of ^{60}Co is usually higher than that of ^{137}Cs and this could be explained by the fact that cesium is present in the aqueous solution as a free hydrated cations (Cs^{+}) with little or nearly no tendency to form soluble complex. On contrary Co^{2+}, as a vital element for plants, has a great liability to form organic and inorganic compounds within the plant cells[7]

Although the removal percentages of ^{60}Co by *Veronica anagallis-aquatica (L.)* as an aquatic plant were very high when present mixed with ^{137}Cs in the same waste solution, the percentage of its removal was increased if the radiocobalt present lonely in the aqueous solution (Figure 5). This observation could be probably due to the fact that Co^{2+} plays an essential role in the growth of numerous plants including the aquatics[9,10]. On the other hand, neglected variation in ^{137}Cs bioaccumulation was found when cesium present as mixture with ^{60}Co or present as alone. This may be attributed to the radiotoxic effect of ^{137}Cs as previously stated[8].

It could be concluded that ^{60}Co has been strongly accumulated in presence or absence of ^{137}Cs with little bit enhancement in the absence of cesium while non-visible change was observed for the absorption of ^{137}Cs if present alone or as a mixture with ^{60}Co in the waste solution. These results may confirm the essential role of cobalt as micronutrients, and the radiotoxic effect of radiocesium.

The light effect on the bioaccumulation efficiency

Environmental factors like light may affect phytoremediation technology of aquatic plants. Three batches of plants each of them consists of 5gm of Veronica were added in glass jars containing simulated radioactive waste solution of nearly the same initial activity concentrations. One batch was grown under direct sunlight; the other was left at the shed light while the last one was left in dark place. The remaining total radioactivity in the solution at different time intervals for the three batches was counted alternatively and the data obtained were represented in Figure 6.

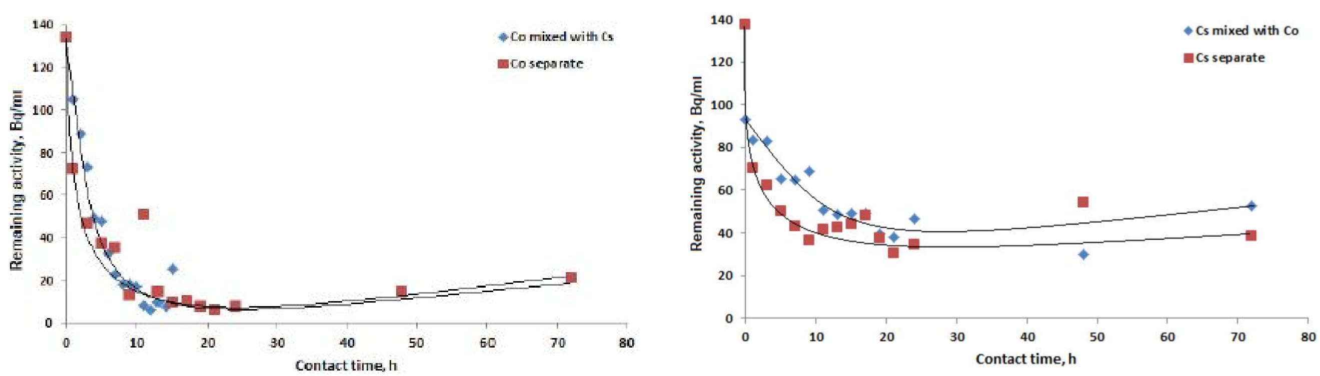

Figure 5: The uptake value as a functions of ^{60}Co and ^{137}Cs found in the waste streams individually or in mixture

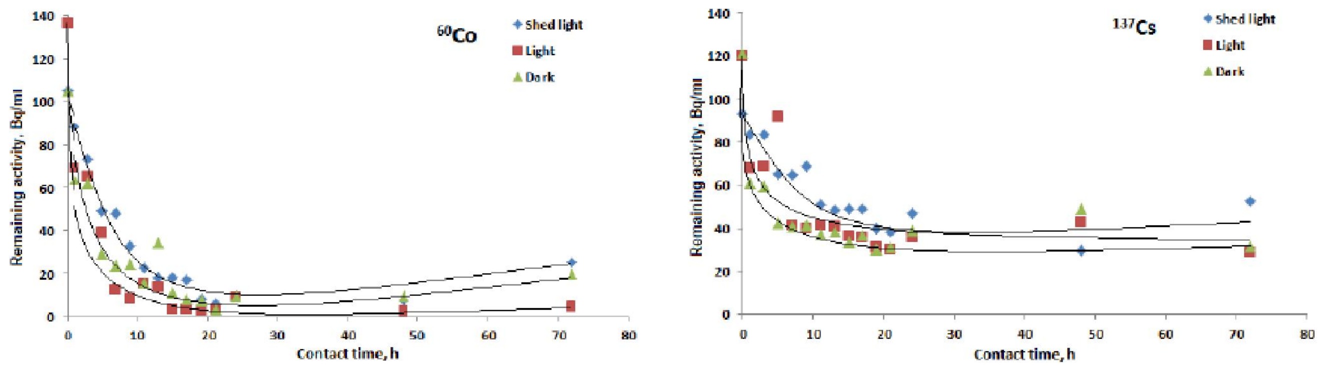

Figure 6: Light effect on the uptake of ^{60}Co and ^{137}Cs from their mixed solution

The maximum bioaccumulation efficiency of radioactive contaminants was reached after the first day of immersion process for the three conditions. However, the rate of removal of ^{60}Co is high under sunlight exposure compared to that present at the shed light or under dark. This behavior could be explained by the light sensitivity of the plant accompanying with the increase in the ability of removing radionuclides present in the waste solution under exposure to direct sunlight. On the other hand, non-considerable variation could be investigated in case of ^{137}Cs bioaccumulation process. Moreover, direct sunlight showed a detectable resistance of the plant against the back release of the two radionuclides and gave more life time for plants immersed in aqueous solutions included radionuclides. These results could be explained by the relation exists between the photosynthesis and the mechanism of the radioactive bioaccumulation. Where the plant in sun light is having a rapid growth and vegetative reproduction rates due to the ultraviolet radiation resulted in fast profilteration which effectively increased the bioaccumulation of the radioactive contaminants[17]. On the other hand, at darkness, low rate of the plant bioactivities may persist and radionuclides uptake was much slower[18].

Concentration ratios (CR) and transport indices (TI) for Veronica plant

The accumulation of radionuclides by edible aquatic organisms is a dynamic process; many contaminant bioaccumulation models assume that the aquatic organisms are in equilibrium with reference media, such as water or sediments. In such models, radionuclide accumulation in aquatic biota can be represented by simplified ratios that relate radionuclide concentrations in biotic tissues to concentrations in the reference media[19].

TABLE 2 represents the concentration ratios and transport indices data for ^{60}Co and ^{137}Cs through the Veronica tissues. It is shown that the radiocobalt is concentrated within the plant more than radiocesium. This again fortified the essentiality of cobalt to the plant

TABLE 2: Concentration ratios and transport indices for ^{60}Co and ^{137}Cs.

Parameters	^{60}Co	^{137}Cs
Initial activity in waste solution, Bq/ml	73	90
Activity content in the dry whole plant, Bq/g	1550	1098
Activity content in dry shoot, Bq/g	42.4	116.9
Activity content in dry root, Bq/g	2077	1437.8
CR, l/kg	20.7	12
TI, %	2.8	11

compared to the cesium. Here it should be noted that Veronica is characterized by high CR for both ^{60}Co and ^{137}Cs compared to *Epipremnum aureum* as terrestrial plant[7], while a large concentration ratio implies better phytoremediation capability. This result approves that *Veronica anagallis-aquatica* plant is suitable for phytoremediation of ^{60}Co and/or ^{137}Cs from their aqueous radioactive waste stream. Based on the TI data, it can be stated unequivocally that Cs^{+} is transported from the root to the shoot is about 4 times faster than Co^{2+} which may be referred to high solubility of the cesium relative to cobalt.

CONCLUSION

The submitted work provides an introduction for cost effective, natural and environmental friendly clean up technology based on the capability of the floating plants, *Veronica anagallis-aquatica (L.)*, to treat waste stream simulates contaminated with ^{60}Co and/or ^{137}Cs. The proposed trial was developed to overcome the drawbacks of the well-known conventional treatment methods. The process was carried in vivo laboratory scale experiments and is considered as a promising technique for bioaccumulation and biostabilization of radiocontaminants from low and intermediate level liquid wastes. The results of the present study therefore indicate that *Veronica anagallis-aquatica (L.)* may be a candidate plant with a high potential for phytoremediation of ^{60}Co and/or ^{137}Cs contaminated streams.

REFERENCES

[1] S.Singh, S.Eapen, V.Thorat, C.P.Kaushik, K.Raj, S.F.D'Souza; Phytoremediation of 137cesium and 90strontium from solutions and low-level nuclear waste by *Vetiveria zizanoides*, Ecotoxicology and Environmental Safety, **69(2)**, 306-311 **(2008)**.

[2] H.M.Saleh; Water hyacinth for phytoremediation of radioactive waste simulate contaminated with cesium and cobalt radionuclides, Nuclear Engineering and Design, **242**, 425-432 **(2012)**.

[3] D.J.Kang, Y.J.Seo, T.Saito, H.Suzuki, D.Y.Ishii; Uptake and translocation of cesium-133 in napiergrass (*Pennisetum purpureum* Schum.) under hydroponic conditions, Ecotoxicology and Environmental Safety, **82**, 122-126 **(2012)**.

[4] S.Singh, V.Thorat, C.P.Kaushik, K.Raj, S.Eapen, S.F.D'Souza; Potential of *Chromolaena odorata* for phytoremediation of 137Cs from solution and low level nuclear waste. Journal of Hazardous Materials, **162**, 743-745 **(2009)**.

[5] S.Eapen, S.Singh, V.Thorat, C.P.Kaushik, K.Raj, S.F.D'Souza; Phytoremediation of radiostrontium (90Sr) and radiocesium (137Cs) using giant milky weed *(*Calotropis gigantea R. Br.*)* plants. Chemosphere, **65**, 2071-2073 **(2006)**.

[6] S.Singh, S.Eapen, S.F.D'Souza; Cadmium accumulation and its influence on lipid peroxidation and antioxidative system in an aquatic plant, Bacopa monnieri L. Chemosphere, **62**, 243-266 **(2006)**.

[7] H.A.Kamel, S.B.Eskander, M.A.S.Aly; Physiological response of *epipermnum aureum* for cobalt-60 and casium-137 translocation and rhizofilteration. International Journal of Phytoremediation, **9**, 403-417 **(2007)**.

[8] J.H.Lee, L.R.Hossner Jr., M.Attrep, K.S.Kung; Uptake and translocation of plutonium in two plant species using hydroponics. Environmental Pollution, **117**, 61-68 **(2002)**.

[9] J.W.Moore; Inorganic contaminants of surface water: Research and monitoring priorities. Springer-Verlag, New York, 98-108 **(1991)**.

[10] P.J.White, M.R.Broadley; Mechanisms of Cesium uptake by plant, New Phytologist, **14**, 241-256 **(2000)**.

[11] M.W.Jayaweera, J.C.Kasturiarachchi, R.K.A.Kularatne, S.L.J.Wijeyekoon; Contribution of water hyacinth (*Eichhornia*, *Crasipes* (Mart) solms) grown under different nutrient conditions to Fe removal mechanisms in constructed wetlands, Journal of Environmental Management, **87**, 450-460 **(2008)**.

[12] P.G.C.Campbell; Interactions Between Trace metals and Aquatic organisms: A Critique of the Free-ion Activity Model, in A.Tessier, D.R.Turner (Eds); Metal Speciation and Bioavailability in Aquatic Systems, John Wiley & Sons, Chichester, U.K., 45-102 **(1995)**.

[13] L.Parent, P.G.C.Campbell; Aluminium bioavailability to the green alga *Chlorella pyrenoidosa* in acidified synthetic soft water, Environmental and Toxicology Chemistry, **13**, 587-598 **(1994)**.

[14] T.B.Kinraide; Use of a Gouy-Chapman-Stern model for membrane-surface electrical potential to interpret some features of mineral rhizotoxicity, Plant Physiology. **106**, 1583-1592 **(1994)**.

[15] Q.Lu; Evaluation of aquatic plants for phytoremediation of eutrophic stormwaters, Ph.D. Thesis, University of Florida, Department of Soil and Water Science, **(2009)**.

[16] A.S.El-Gendy, N.Biswas, J.K.Bewtra; A floating aquatic system employing water hyacinth for municipal landfill leachate treatment: effect of leachate characteristics on the plant growth, Journal of Environmental Engineering and Science, **4(4)** 227-240 **(2005)**.

[17] M.Mkandawire, E.G.Dudel, Accumulation of arsenic in L.Lemna gibba (duckweed) in tailing waters of two abandoned uranium mining sites in Saxony, Germany, Science of the Total Environment, **336**, 81- 89 **(2005)**.

[18] R.Scott; A study of caesium accumulation by marine algae, In: Radioisotope conference, Butterworth Publications, London, **1**, 273-379 **(1954)**.

[19] International Atomic Energy Agency (IAEA), Handbook of parameter values for the prediction of radionuclide transfer in terrestrial and freshwater environments, Technical Reports Series 472, **(2010)**.