Sorption Studies of Radionuclides from Simulated Low Level Waste using Green Biosorbent

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Abstract
In view of the disadvantages associated with conventional methods for metal removal, there is a need for alternative, cost-effective technologies. In recent years, biosorption process has been considered as an efficient and eco-friendly alternative treatment technology for the removal of metals from radioactive wastes. The subject matter of this study is to evaluate a natural, viable and low-cost adsorbent – Dry Cowdung Powder (DCP), for the removal of $^{137}Cs(I)$ and $^{60}Co(II)$ from simulated low level radioactive waste. Experimental parameters like pH, sorbent dosage, contact time and temperature of the sorption process were optimized and maximum uptake of 66% and 90% was observed for Cs(I) and Co(II) respectively.

This green technique was further employed to check the effect of different salts on the biosorption process of both the metal ions applying Hard and Soft Acid Base (HSAB) theory. Metal ions and salts were categorized into hard and soft acids and bases to understand the reaction mechanism of biosorption process. Thermodynamic parameters such as ΔG˚, ΔH˚ and ΔS˚ determined the exothermic nature of the process with an enthalpy change of -4.18 kJ.mol^{-1} and -2.70 kJ. mol^{-1} for Cs(I) and Co(II) respectively. This method possesses rapid kinetics, thus the process was time and energy efficient.

Keywords: Dry Cowdung Powder, Biosorption, Green Technique, Thermodynamics, HSAB Theory.

Introduction
Radioactive waste can remain hazardous for a few days or for thousands of years depending upon their radioactive half-lives. Treatment of this waste is an important objective to ensure that the radiation exposure to an individual and the environment does not exceed the prescribed limit. Solvent extraction, chemical precipitation, ion exchange, membrane process, solar evaporation and sorption are conventional and recently developed methods reported for treatment of radioactive waste[1]. This study is focused on removal of Cs(I) and Co(II) ions from simulated low level radioactive wastes by biosorption process using green biosorbent - Dry Cowdung Powder (DCP).

^{137}Cs is produced by the fission of uranium and is not a naturally occurring radionuclide. Nuclear reactor operations form the largest source of ^{137}Cs. It has a half-life of 30.17 years and it emits one to two high-energy beta particles. Approximately 85% of all ^{137}Cs decays result in the emission of a 0.662 MeV gamma ray[2,3]. ^{60}Co is the most stable radioactive isotope of cobalt with 5.27 years of half-life. It is produced in the structural steels and other alloys of nuclear reactor vessels and internal components from neutron activation of ^{59}Co. It emits two highly energetic gamma rays of 1.17 MeV and 1.33 MeV and poses an external exposure hazard[4].

Biosorption process has long been investigated by most researchers using different types of biomass for the removal of Cs(I) and Co(II) from aqueous media. For example activated sludge[5], microalgae haematococcus pluvialis and chlorella vulgaris[6], porous tuff[7], extracted chitosan[8], bacteria isolated from spent nuclear fuel pools[9], lemna gibba[10], spent black tea (camellia sinensis)[11] are the biological materials that have been used for the uptake of Cs(I) and Co(II) from waste waters.

Literature review reveals the characterization studies of DCP carried out by previous researchers[12,13]. It sheds light on the acidic and basic moieties present on the surface of the biosorbent which act as active sites for bonding. DCP has been employed without any pretreatment. This inactive non-living biomass has an inherent property to bind and concentrate metal ions from aqueous surrounding which enables faster and easier adsorption[14].

Material and Methods
Radiotracer technique has been used for the quantification of results in which small amount of radioactive isotope is added in order to trace the chemical reaction of a certain element in the system. The amount of a radioactive tracer necessary for an experiment is normally so small that no detectable radiolysis occurs in the system[15]. Radioisotopes employed as tracers were obtained from the Board of Radiation and Isotope Technology (BRIT), Trombay, Mumbai. The chemicals used for the experimental work were of A. R. grade. Dry Cow Dung (100 mesh) was provided by Keshav Shrushti Research Centre (Thane, India) and due precautions were taken to avoid contaminations.

Low level radioactive waste composition was obtained from Tarapur Power Plant and batch solutions were prepared containing Cs(I), Sr(II), Co(II), NaI and $NaNO_3$. Radioactive ^{137}Cs and ^{60}Co were added to the respective solutions which were then mechanically agitated with known amount of DCP and 15 mL of final volume. The resultant solution was

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centrifuged and the activity present in the supernatant was measured using Single Channel NaI(Tl) well-type gamma ray spectrometer (Type GRS 101P, model No. 013, PLA Make). The activity was measured by taking an aliquot from the supernatant which is related to percentage biosorption as follows:

$$\text{Percentage biosorption} = \frac{A(i) - A(f)}{A(i)} \times 100 \quad (1)$$

where A(i) = initial activity taken and A(f) = final total activity in supernatant.

Experimental parameters like pH, sorbent dosage, contact time and temperature of the sorption process were optimized at maximum uptake of Cs(I) and Co(II).

Results and Discussion

Influence of pH: Solution pH influences the dissociation of functional groups on the active sites of the biosorbent and the solution ion chemistry. For Cs(I), it is perceived that the biosorption gradually increases and in the reactor range of pH 7.5 to 8.5, maximum biosorption is 66.81% as shown in figure 1. It was observed that DCP was effective for the removal of Co(II) over the pH range of 1–10 and the biosorption of Co(II) was fairly independent of pH. Thus, the system would work well at acidic, neutral and alkaline ranges. Maximum biosorption of 92% for Co(II) was achieved at pH 8.5. Thus, pH 8.5 was chosen for both the metal ions in order to avoid precipitation of metal hydroxides.

Effect of adsorbent dosage: On increasing the adsorbent amount, increase in adsorption percentage has been obtained. This is due to an increase in the available adsorption sites on DCP. From figure 2, it can be seen that maximum adsorption of 66.31% was achieved for Cs(I) with 33.33 g/L of DCP (or 500 mg) and 91% of Co(II) with 13.33 g/ L of DCP (or 200 mg). Further addition of adsorbent does

not affect the percentage biosorption, as it remains almost constant.

Effect of Contact Time: Figure 3 revealed that 5 mins of contact time was sufficient to get maximum biosorption of 66% and 92% for Cs(I) and Co(II) respectively. The rate of Cs(I) and Co(II) biosorption on DCP was very rapid. Further increase in time does not affect percentage sorption as it increases very gradually. The adsorption process achieved equilibrium within 5 mins for both the metal ions due to the availability of the surface sites on DCP.

Effect of temperature: Temperature plays a vital role in the process of biosorption, it is generally assumed that biosorption is carried out between 20° and 35°C. It was reported that 66% of Cs(I) and 91% of Co(II) was adsorbed by DCP at 303 K after 5 mins of contact time as shown in figure 4. As the temperature increases, a decrease in biosorption has been recorded, this is because an increase in temperature weakens the attractive forces between biomass surface and metal ions.

Thermodynamics: Thermodynamic parameters such as Gibbs free energy change $\Delta G°$, enthalpy change $\Delta H°$ and entropy change $\Delta S°$ were calculated from the following equations[16]:

$$\Delta G° = - RT \ln K_a \quad (2)$$
$$\Delta G° = \Delta H° - T\Delta S° \quad (3)$$

According to Vant Hoff's equation:
$$\ln K_a = \Delta S°/R - \Delta H°/RT \quad (4)$$

where K_a is the adsorption equilibrium constant, R is the gas constant (8.314 J/mol.K) and T is the absolute temperature (273 K). A graph of $\ln K_a$ versus $1/T$ was plotted as seen in figure 5. The values of $\Delta H°$ and $\Delta S°$ were evaluated from the slope and intercept of Vant Hoff's plot as displayed in figure 5 and table 1.
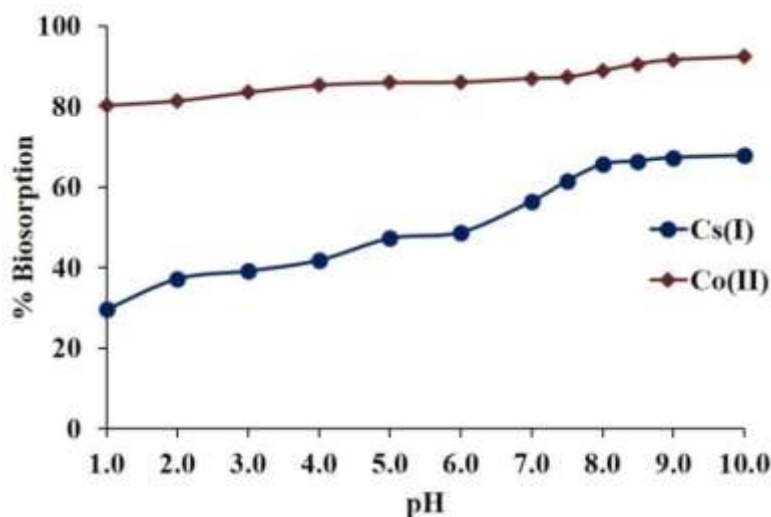

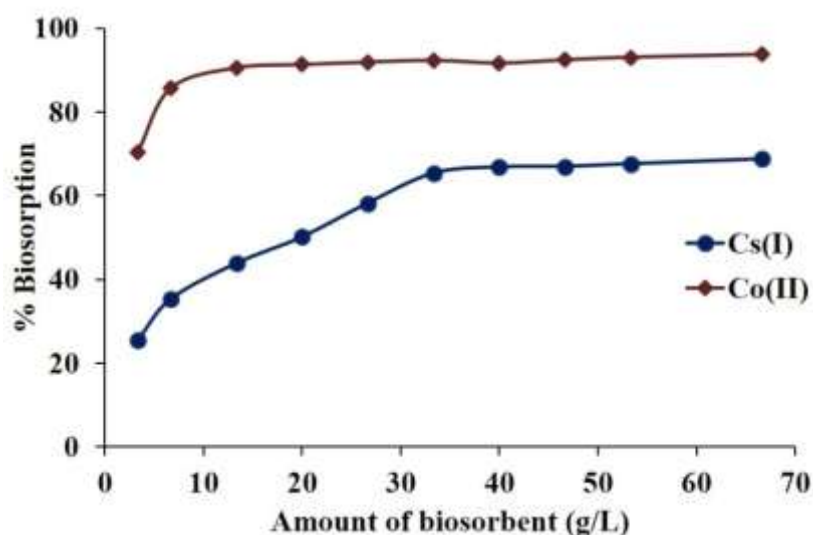**Figure 1: Effect of pH on biosorption of Cs(I) and Co(II)**

Figure 2: Effect of adsorbent dosage on biosorption of Cs(I) and Co(II)
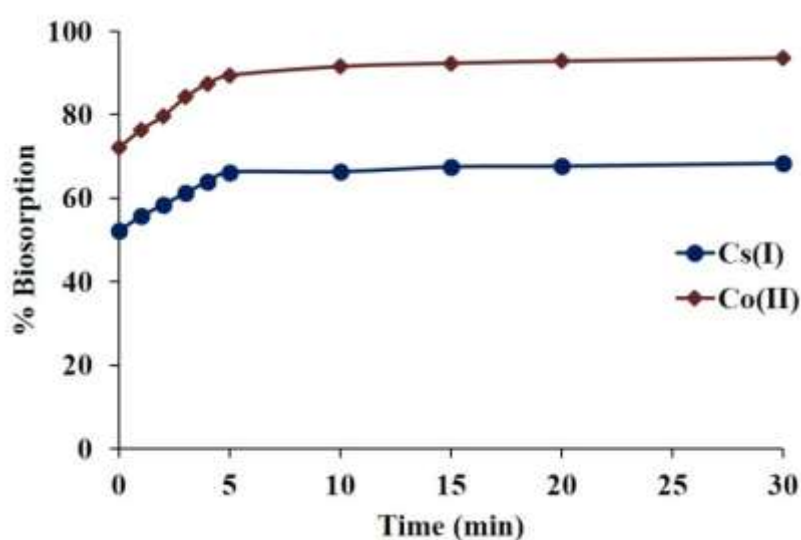

Figure 3: Effect of contact time on biosorption of Cs(I) and Co(II)
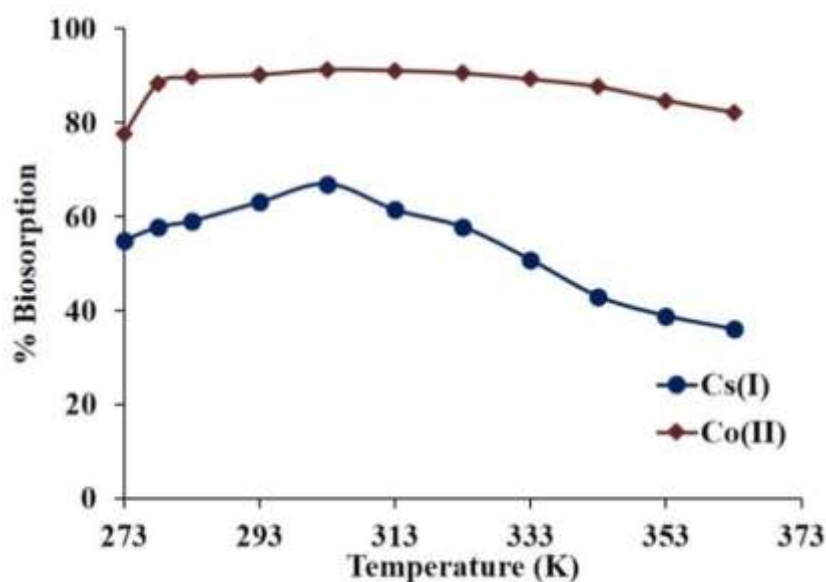

Figure 4: Effect of temperature on biosorption of Cs(I) and Co(II)

Thermodynamic considerations dictate that the ΔG° value is the fundamental criterion for determination of adsorption process characteristics. As seen from table 4, the ΔG° value was calculated to be negative which indicated the spontaneous and feasible nature of both Cs(I) and Co(II) adsorption by DCP. The negative value of ΔH° suggested the adsorption to be exothermic. Also, the positive value of ΔS° described the randomness of the adsorption process along with the affinity of the adsorbent for metal ions.

HSAB theory for biosorption of Cs(I) and Co(II) in presence of different salts: After successful achievement of biosorption of Cs(I) and Co(II), the metal ion biosorptions were studied in the presence of different ionic salts to observe the interference of the same. The selectivity of DCP biosorption in presence of these salts towards Cs(I) and Co(II) is explained by this data. Concentrations of 10, 25, 50 and 100 mg of salts were experimented along with metal ions of interest in aqueous media with only carrier solution and respective isotopes. To study the interference of different salts Hard and Soft Acid Base theory was applied.

According to HSAB theory, metal ions act as Lewis acids and ligands act as Lewis bases. Hard acids tend to form a strong bond with hard bases and soft acids with soft bases. Cs(I) is soft acid or soft ion and hence has higher affinity to bind readily to soft bases. Co(II) is a borderline acid and hence its characteristics of borderline acids are intermediate between those of hard acids and soft acids[17]. Effect of salts on the biosorption of Cs(I) and Co(II) is shown in table 2.

From the table 2, it was observed that the use of different salts in the biosorption process was affected by increasing or decreasing the percentage biosorption with an increasing concentration of salts. Some salts proved to be non-interfering at 100 mg whereas some profoundly suppressed the adsorption process even at 10 mg. An increase in concentration of ligand decreases the percentage adsorption due to readily forming stable metal-ligand complexes or due to competition between metal ion and ligand for sorption sites on the adsorbent.

In the case of Cs(I), salts like citrate, iodate, thiosulphate and hydroxide do not affect the biosorption at 10 mg concentration, however, soft bases like thiourea and iodide react with Cs(I) and aid the biosorption process. However at 100 mg concentration, iodide suppresses the biosorption of Cs(I) by ~10%.

Table 1
Thermodynamic constants for the biosorption of Cs(I) and Co(II) on DCP

Elements	ΔH° (kJ.mol^{-1})	ΔS° (J.mol^{-1}K^{-1})	ΔG° (kJ.mol^{-1})	R^2
Cs(I)	-4.18	16.02	-0.77	0.823
Co(II)	-2.70	17.22	-2.57	0.884

Table 2
Interfernce of diffent salts on biosorption of Cs(I) and Co(II)

| Interference of salts	Concentration of salts	Cs(I)			Co(II)		
		Hard Base	Soft Base	Borderline Base	Hard Base	Soft Base	Borderline Base
Interfering	10 mg	Sulphate, chromate, dichromate, bicarbonate, chloride		Bromide, nitrite,	Chromate, dichromate, bicarbonate,		Citrate
	100 mg	Hydroxide, phosphate, tartarate, nitrate, carbonate, chlorate, acetate,	Iodate	Sulphite, citrate, thiosulphate	Hydroxide, phosphate, carbonate, acetate,	Iodide	Sulphite, thiosuphate
Non-interfering	100 mg		thiourea, iodide		Sulphate, nitrate, chlorate, tartarate, chloride	Iodate, thiourea	Bromide, nitrite,
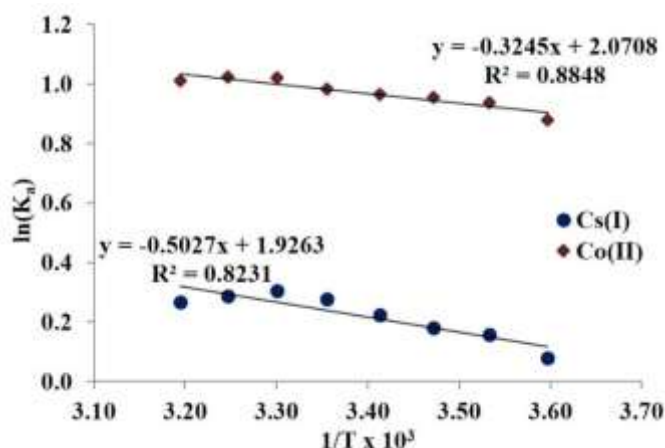
Figure 5: Thermodynamic parameters for the biosorption of Cs(I) and Co(II) on DCP

Salts like phosphate, chloride, sulphate, nitrate, dichromate, bromide, nitrite, chromate and chlorate interfere with the biosorption process by decreasing percentage biosorption at 10 mg of concentration. Hard bases like phosphate, chloride, sulphate, nitrate, dichromate, chromate and chlorate also interact with soft acid Cs(I) which can be attributed to valency charges. Thus, HSAB theory does not apply for the bond formation between metal ion and these ligands. On the other hand, nitrite and bromide fall into the borderline base category, thus their interaction with Cs(I) suppresses its biosorption.

In the case of Co(II), table 2 indicates that the presence of salts like tartarate, thiosulphate, thiourea, chloride, iodate, sulphate, nitrate, nitrite, bromide, hydroxide and chlorate does not have significant effect on Co(II) biosorption at 10 mg of concentration. An increase in concentration of these ligands does not affect the percentage adsorption except for hydroxide. According to HSAB theory, Co(II) is a borderline acid and hence, the characteristics of borderline acids are intermediate between those of hard acids and soft acids. Hence, borderline acid Co(II) can easily interact with hard and soft bases.

Iodide being a soft base, aids the biosorption at initial concentration of 10 mg and further rise in concentration of iodide decreases the biosorption. Citrate proved to be an interfering agent. It profoundly suppressed the adsorption process even at 10 mg from 84% to 36%. Salts like hydroxide, phosphate, sulphite and carbonate were interfering at 100 mg concentration.

Conclusion
The potential of DCP to sequester metal ions Cs(I) and Co(II) has been successfully demonstrated employing tracer technique. Maximum adsorption of 66% and 90% was achieved in 5 mins of contact time and at room temperature for Cs(I) and Co(II) respectively. Thermodynamic study showed that the adsorption process for both metal ions Cs(I) and Co(II) was feasible and spontaneous, increase in randomness achieved with increase in temperature and the degrees of free active sites increased at the solid–liquid interface during the adsorption process. The process was exothermic with negative $\Delta H°$ values. Also, interference of different ionic salts in both metal ion biosorption has been successfully studied.

Metal ions and salts were categorized into hard and soft acids and bases which helped to understand the reaction mechanism of biosorption process. The study offers successful adsorption of Cs(I) and Co(II) from simulated low level waste with optimized parameters and explained the reaction thermodynamics for both the metal ions. It also provided detailed information about sequestering behavior of DCP in presence of different salts. As DCP was used without any pretreatment procedures, it offers a low cost alternative with rapid adsorptive ability as a promising technique for low level radioactive and industrial wastewater clean-up.

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