

Biosorption of Cs (I): Utilization of an eco-friendly adsorbent Dry Cowdung Powder

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Abstract:

Dry Cowdung Powder (DCP) – a green biosorbent, has been demonstrated for Cs(I) removal from aqueous media using radiotracer technique. 100 mesh DCP was added to Cs(I) carrier solution spiked with radioactive Cs-137. Parameters like pH, biosorbent dose, agitation speed, contact time, temperature and Cs(I) ion concentration were optimized. Industrial effluents or other polluted water bodies contain different salts in varying proportions. To analyse the effect of these salts on adsorption of Cs(I), various sodium, potassium and ammonium salts were used. DCP characteristics pre and post biosorption of Cs(I) was analysed with EDAX spectra. The investigation reports a successful Cs(I) metal removal by following the principles of green chemistry.

Keywords: Dry Cowdung Powder, Cs-(I), Biosorption, Pseudo-Second-Order

Introduction

Treatment of a liquid waste using ecofriendly techniques is the focus of modern times. As the metallic content increases, the toxicity of the effluent increases and impacts the environment severely. Cs(I) is an alkali metal like potassium which can be easily taken up by humans through the digestive tract. Cs(I) tends to concentrate in muscles due its similarity to K(I), and gets eliminated from the body fairly quickly. We have applied radiotracer technique for Cs(I) removal using Cs-137 as a radiotracer of interest as it takes major part in radioactive wastes and aqueous waste from different industries.

There are number of techniques applied over the years for separation studies, such as ion exchange, chemical precipitation, membrane process, and liquid extraction. These have certain shortcomings like partial metal removal, higher energy and reagent requirements, production of hazardous waste materials, and their disposal treatment. The biosorption technique follows green chemistry principle for effluent clean up. Biosorption is the physico-chemical interaction between dead biomass and pollutants and is faster compared to bioremediation, due to passive binding. Plant biomass and microbes like marine algae, *Rhodospiridium fluviale*, *Ocimum basilicum*, *Azolla filiculoides*, coir pith, arca shells and minerals like illite have previously been used for Cs(I) removal from different matrices¹⁻³. Thus, the aim of this work is the biosorptive removal of Cs(I) using DCP for wastewater remediation.

Freely available non living biomass DCP holds natural adsorption properties owing to the presence of humic acid, fulvic acid and bile pigments, proteins and fats etc. DCP binds and concentrates metallic pollutants from the surroundings without any external energy which makes the process kinetically faster and cost effective. Radiotracer technique simplifies the process without any radiolysis effect. It requires a very small amount of radioisotope for elemental detection.

Experimental:

- DCP was procured from Keshav Shristi Research Centre, Bhayander, India, with size of 100 mesh and is from a single source origin which is used throughout the experimental parameters.
- The Radiotracer ¹³⁷Cs(I) was obtained from BRIT (Board of Radiation and Isotope Technology, Mumbai, India). Strength of Cs tracer used was 0.25 micro curie and 1 mL of this solution was used as tracer for all experiments.
- **Batch Biosorption:** DCP in known amount was added to 15 mL of solution containing 1 mL of ¹³⁷Cs(I) tracer, 1mg of Cs(I) carrier and pH adjustment was done using dil. HNO₃ to maintain homogeneity across all parameters for the experiment. Nitrates formed are soluble in water and would still interact with the adsorbent. And for basic range dil. NaOH was used. To achieve equilibration, the resultant solution was mechanically stirred for required time and then centrifuged. The final activity

was measured with a NaI(Tl) well-type gamma-ray spectrometer (GRS). Experimental parameters like pH (1 to 10), Cs(I) ion concentration (0.5 – 20 mg/mL), contact time (0 – 30 min), agitation speed (0 – 4000 rpm), adsorbent dose (6.67 – 46.67 g/L), temperature (283–363 K), have been optimized for developing an efficient process. The reaction mechanism was investigated by applying kinetic, isotherm and thermodynamic modelling. Reproducibility has been checked in triplicate. The percentage biosorption was calculated using following formula:

$$\% \text{ Adsorption} = \frac{A(i) - A(f)}{A(i)} \times 100 \quad \dots(1)$$

Where, A(i) = Initial Activity, A(f) = Final Activity in supernatant

Results and Discussion

All parameters have been comprehensively studied in possible experimental range for optimization of all parameters.

1. Effect of solution pH

The overall surface charge of an adsorbent can be controlled by modifying the solution pH over a broad range. Both Cs(I) and DCP behave as oppositely charged adsorbate and adsorbent which increases the electrostatic force of attraction between them and results into biosorption of Cs(I) on DCP. The result of pH variation is shown in **Fig. 1**. As pH increases, percentage adsorption rises and attains a plateau between pH 4 to 6, this may be due to no change in the ligand binding to Cs in this pH range. It is known that DCP being heterogeneous in nature, ligand binding may change with change in pH. Optimum pH of Cs(I) sorption was found at pH 7 for the maximum biosorption of 43% of 1 mg/15mL of Cs(I) and the adsorption remains at a plateau between pH 7 to 10. More negatively charged active sites become available as pH increases, thus facilitating greater metal uptake⁴. The formation of a plateau can be attributed to the saturation in available sites for binding.

2. Effect of adsorbent dose

Varying the adsorbent dose from low to high amount increases the adsorption till the system achieves equilibrium due its direct proportionality to surface area available. Equilibrium is achieved after 40 g/L and further addition does not increase the biosorption due to interaction

and aggregation of adsorbent sites. Our results from **Fig. 2** suggest that by employing 40 g/L of DCP 42.89% of Cs(I) was successfully removed.

3. Effect of Temperature

Biosorption process has been reported exothermically ⁵ in nature thus temperature is an important aspect in adsorption. It is observed from **Fig. 3** that Cs(I) biosorption increases as temperature increases and is maximum at 303K. As temperature is increased further it exhibits a negative impact and a decrease in sorption was observed. The maximum thermal energy weakens the bond between Cs(I) and DCP which can further be applied for desorption studies.

Table 2 gives optimized parameters for maximum bioabsorption of Cs(I).

4. Effect of Salts

The effect of different organic and inorganic salts on biosorption process is an important part due to the presence of these salts in polluted waters or in industrial effluents. Biosorption experiments were performed at different salt concentration like 10, 25, 50 and 100 mg, keeping the optimized parameters constant. Biosorption behaviour was seen in **Table 1** with different salts in which some salts suppress adsorption with low concentration and some act as non-interfering at high concentration of 100 mg.

An increased ligand concentration decreases the adsorption because of a stable metal-ligand complex being formed or competition between the metallic ion and ligand for sorption sites on the adsorbent. 100 mg thiourea and 50 mg acetate and citrate were non-interfering hence these salts can be used for separation of Cs(I) from other metallic ions which get suppressed by these ligands. At a concentration of 10 mg, chloride, chromate, dichromate, phosphate and nitrite salts interfered with Cs(I) biosorption. Their effect was overcome by doubling the DCP dosage. For separation studies, these salts may be employed as masking agents depending on their affinities for other metal ions.

5. Thermodynamic Parameters

The spontaneity of the reaction has been analysed using thermodynamic parameters. A negative change in Gibbs free energy ΔG^0 , suggests the spontaneity of a chemical reaction. And both energy and entropy factors must be considered to calculate ΔG^0 of a process.

Reactions occur spontaneously at a given temperature if ΔG^0 is negative⁶⁻¹⁰. ΔG^0 is calculated by the equations:

$$\Delta G = \Delta H - T\Delta S \text{ [Gibbs free energy equation]} \quad \dots(2)$$

$$\Delta G^0 = -RT \ln K_a \text{ [Van't Hoff equation]} \quad \dots(3)$$

Where R = Universal Gas Constant (8.314 J/mol/K), T = Temperature (K), $K_a = C_0/C_e$ (C_0 = activity or conc. of adsorbed metal ion, C_e = activity or conc. of metal ion left in solution at equilibrium)

The standard Gibbs free energy ΔG^0 (kJ/mol), standard enthalpy change ΔH^0 (kJ/mol), and standard entropy change ΔS^0 (J/mol K) were calculated using the above equations.

Combining equation nos. 2 & 3 and rearranging in linear form [$y = mx + c$] as following

$$\ln K_a = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad \dots(4)$$

The values of ΔH^0 and ΔS^0 were computed from the graph of $\ln K_a$ vs. $1/T \times 10^3$ (as seen in **Fig. 4**), to be -35.93 kJ/mol and 112.95 J/mol K respectively. ΔG at 303K was -1.36 KJ/mol, thus negative value confirms the feasible and spontaneous biosorption with high preference of Cs(I) ions for DCP. ΔH^0 is negative, thus the reaction is exothermic and ΔS^0 is positive, which reflects the affinity of adsorbent for Cs(I) ions.

6. Kinetic Parameter

The kinetic biosorption data were obtained by batch experiments by varying the time of reaction from 0 to 30 min. Lagergren pseudo-first-order, Ho & McKay pseudo-second-order and intraparticle diffusion model have been used. From these models, Ho & McKay pseudo-second-order model was the best-fitting¹¹⁻¹³.

The Kinetic data obtained was applied to Ho & McKay pseudo-second-order model as expressed in the equation given below:

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \quad \dots(5)$$

Rearranging Equation 5 in linear form as [$y = mx + c$]

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad \dots(6)$$

Where,

t = time (min)

q_t = amount of metal (mg) adsorbed per gm of adsorbent at time (t)

q_e = Maximum adsorption capacity

K₂ = rate constant (g mg⁻¹ min⁻¹)

The graph of t/q_t versus t is shown in **Fig. 5**. The constants K₂ = -13.75 g mg⁻¹ min⁻¹ and q_e = 0.63 mg/g have been calculated from the graphical equation. The correlation coefficients R² value 0.9995 was close to 1, thus pseudo-second-order kinetics fit the system and the rate-limiting step may be chemical adsorption involving valent forces through sharing or the exchange of electrons between the DCP and monovalent Cs(I) ions.

7. Isotherm profile

Most mathematical biosorption models used in literature describe simple Langmuir or Freundlich sorption isotherms, where the metal binding is determined as a function of its equilibrium concentration in the solution, without reference to pH or competing ions in the same solution system. For this study, both models were applied to the data obtained^{6,14-20}.

Langmuir isotherm model gives the monolayer formation of adsorbate on the outer surface of adsorbent, after this surface interaction no further adsorption occurs and system achieves equilibrium. Thus, it represents the equilibrium distribution of metal ions between the solid and liquid phases.

Linear form [y = mx + c] can be expressed as

$$\frac{1}{q_e} = \frac{1}{K_L Q_0} \frac{1}{C_e} + \frac{1}{Q_0} \quad \dots(7)$$

Where,

C_e = the equilibrium concentration (mg/dm³)

q_e = the amount of metal ion sorbed (mg/g)

Q₀ = q_e for a complete monolayer (mg/g) = Maximum adsorption Capacity

K_L = Langmuir biosorption equilibrium constant (dm³/mg)

R_L is an equilibrium parameter which indicates nature of adsorption, it is an essential feature of the Langmuir model which follows the given characteristics:

if $R_L > 1$ process is Unfavourable,

if $R_L = 1$ process is Linear,

if $0 < R_L < 1$ process is Favourable,

if $R_L = 0$ process is Irreversible⁷.

Where R_L is calculated using the equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad \dots(8)$$

Where,

C_0 = initial concentration (mg/dm³)

K_L = the constant related to the energy of adsorption (Langmuir Constant).

R_L = the value indicates the adsorption nature

Freundlich isotherm can be applied for both monolayer chemisorption process and multilayer adsorption. The Freundlich isotherm can be derived assuming a logarithmic decrease in the enthalpy of sorption with the increase in the fraction of occupied sites. It is expressed as following:

$$q_e = K_F C_e^{1/n} \quad \dots(9)$$

Linear form expressed as $[y = mx + c]$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \dots(10)$$

K_F acts as an indicator of adsorption capacity. Similarly, $1/n$ is an indicator of the strength of adsorption, if $1/n < 1$ it indicates chemical adsorption and explains favourable adsorption at low adsorbate concentration, if $1/n > 1$ it suggests cooperative adsorption and strong attraction between the adsorbate and adsorbent even with high concentration. If $n < 1$ or $n > 1$ it implies chemical and physical adsorption respectively.

The regression coefficient for Langmuir isotherm for Cs(I) biosorption found to be 0.6823 which prove that the system does not fit for the same. From **Fig. 6**, Freundlich constant K_f was 0.12, $1/n$ value was 0.4769, and n was 2.10, with $R^2 = 0.9096$. The best-fitting isotherm

to explain the nature was Freundlich model which indicates that biosorption involves chemical bonding between DCP and Cs(I) and is favourable at low Cs(I) concentration.

8. EDAX Spectra pre and post adsorption

Characterization of the biosorbent is an important step in understanding metal ion and biosorbent bonding mechanism. To study this part, the EDAX spectra has been analysed pre and post sorption. The results suggest the presence of K, Si, Zn, Fe, Ti, Mn on the matrix of DCP from **Fig. 7**. After biosorption, the presence of Cs(I) can be seen on the matrix of DCP along with other elements which indicates the mechanism does not follow ion exchange procedure. The kinetic calculations show that the reaction follows Ho & McKay pseudo-second-order model which suggests a chemical interaction between metal ion and sorption sites of DCP.

Conclusions

All the parameters have been comprehensively studied in possible experimental range for optimization. For biosorption of 1 mg Cs(I) with DCP at solution pH 7, time of contact 5 min, with 40 g/L of DCP, agitation speed 2000 rpm, at 303K, the removal efficiency is about 40-45 %. The modelling parameters were also studied with optimized parameters. Cs(I) is a very weak Lewis acid and has a low tendency to interact with ligands in general, thus making its biosorption a challenging prospect. Study of salts was undertaken to understand their interference and to compile them as possible masking agents for separation studies. The kinetic, thermodynamic and isotherm studies suggested that sorption on DCP was a chemical interaction between Cs(I) and sorption sites of DCP and is a spontaneous exothermic process which was also confirmed by the EDAX studies. The study provides collective data on biosorption of Cs(I) using an eco-friendly biosorbent along with the interference of different salts.

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Figures:

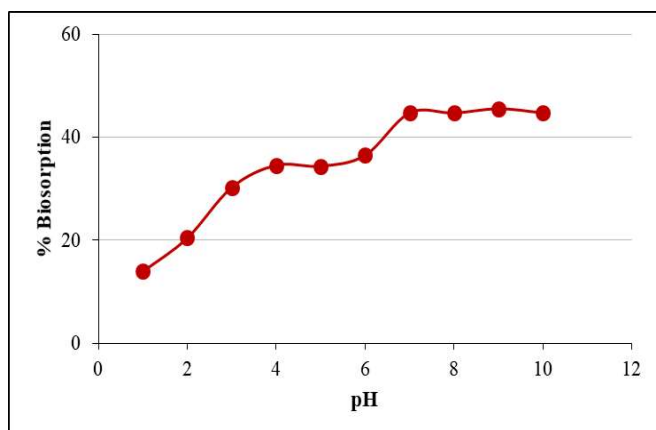


Fig. 1: Effect of solution pH on biosorption of Cs(I)

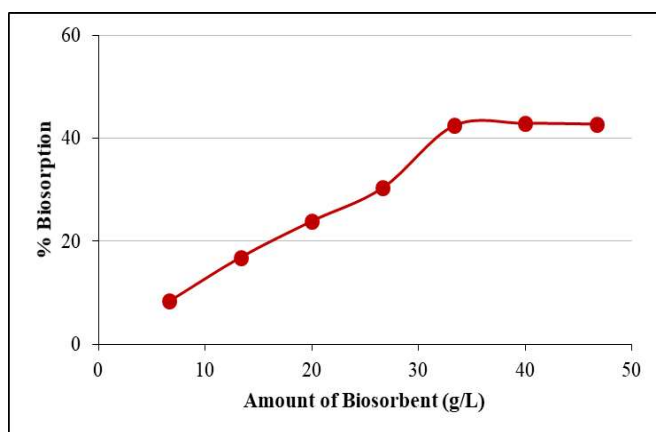


Fig. 2: Effect of adsorbent dose on biosorption of Cs(I)

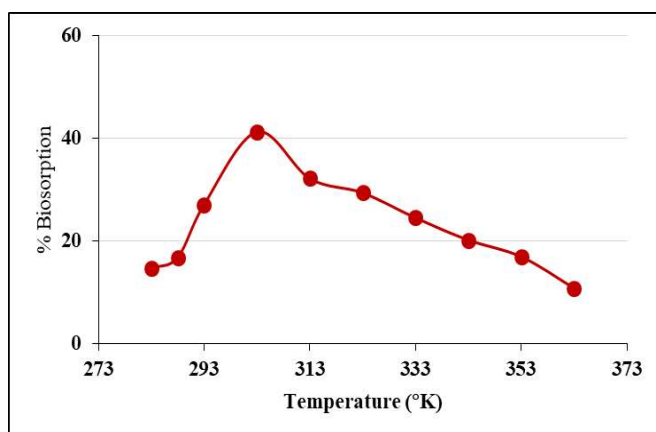


Fig. 3: Effect of Temperature on biosorption of Cs(I)

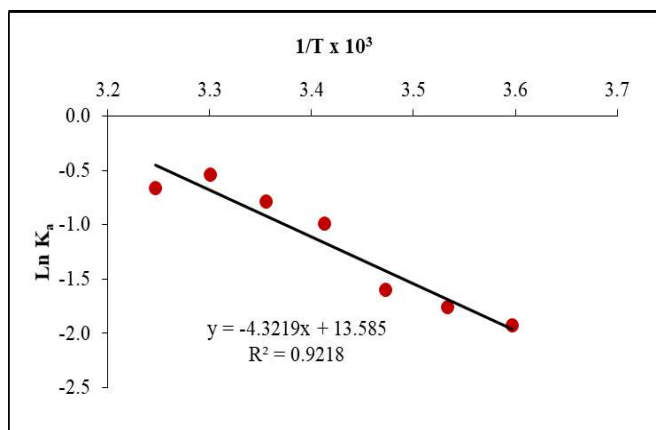


Fig. 4: Thermodynamic graph of $\ln K_a$ vs $1/T \times 10^3$

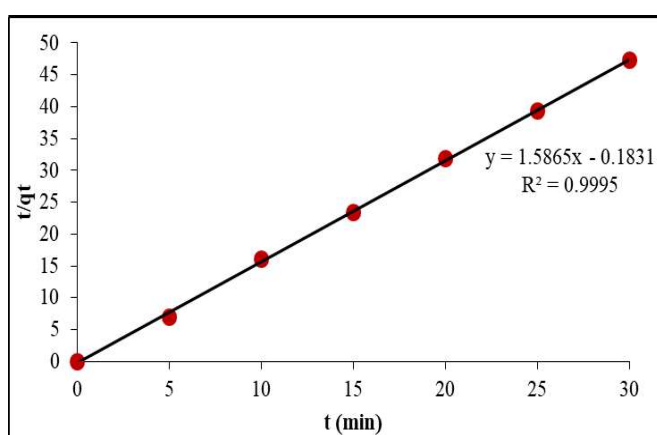


Fig. 5: Ho & McKay pseudo-second order Plot of t/q_t vs t

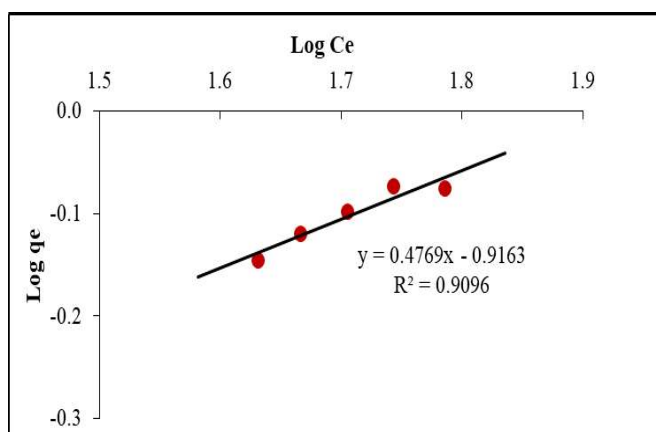


Fig. 6: Freundlich Isotherm Plot of $\log q_e$ versus $\log C_e$

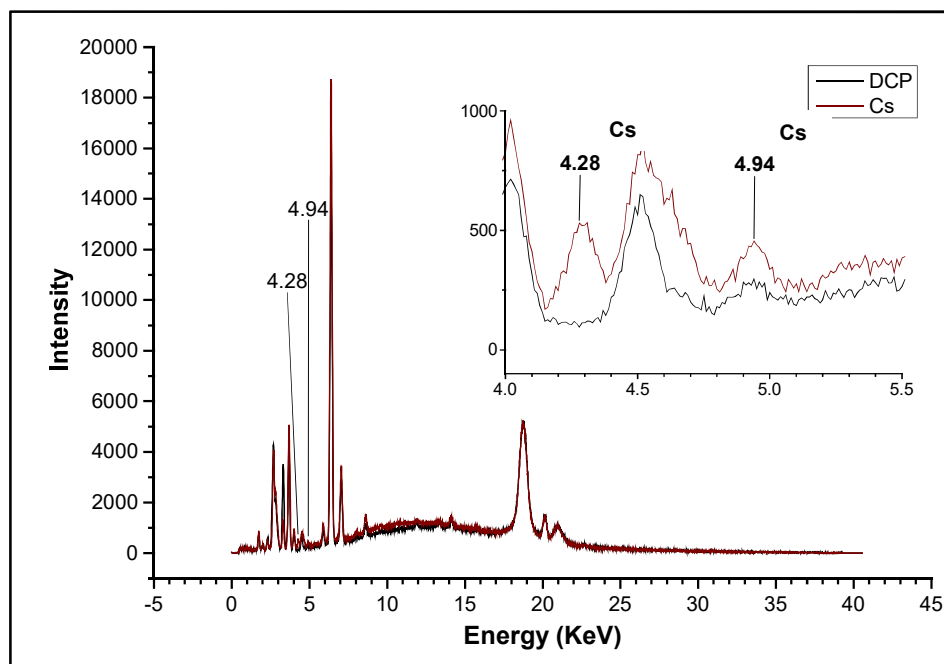


Fig. 7: EDAX spectra of Intensity versus Energy (KeV) of DCP pre and post adsorption of Cs(I)

Tables:

Table 1: Effect of salts on biosorption of Cs(I) under the optimized conditions

Amount of Salt in mg		Salts under study
100	Non-interfering	Thiourea
50	Non-interfering	Acetate, Citrate
25	Non-interfering	Sulphate, Nitrate, Iodate, Carbonate, Thiosulphate, EDTA, Tartarate, Oxalate
10	Non-interfering	Hydroxide, Chlorate, Fluoride, Bicarbonate, Bromide, Sulphite
10	Interfering	Chloride, Chromate, Dichromate, Phosphate, Nitrite

Table 2 Optimized parameters for maximum Biosorption of Cs(I)

pH	7.0
Adsorbent dose	40 g/L
Agitation Speed	2000 rpm
Contact time	5 min
Temperature	303K
% Biosorption	42 – 45 %

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