



vEGU - 2021

SSS7.8 Novel sorbent materials and humic substances for
environmental remediation



SOIL AUGMENTATION BY HUMUS: REPLENISHING LOST SOILS AND SUPPLEMENTING NEW ONES

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Overview



Promote cyclic flow of nutrients



The complex structures of HS bind with xenobiotics like radionuclides, pesticides, heavy metals, industrial dyes thereby acting as **natural sieves**

Biostasy

Periods of soil formation

Soil Supplementation

In addition to routine soil supplementation, HS/HA can be added to regolith simulants that are to be supplemented with organic matter for plant growth studies



Humic Substances (HS) in soil are crucial to life on Earth

- **Competitive Sorption**
- **Metal Binding**
- **Complexation**
- **Water Retention**

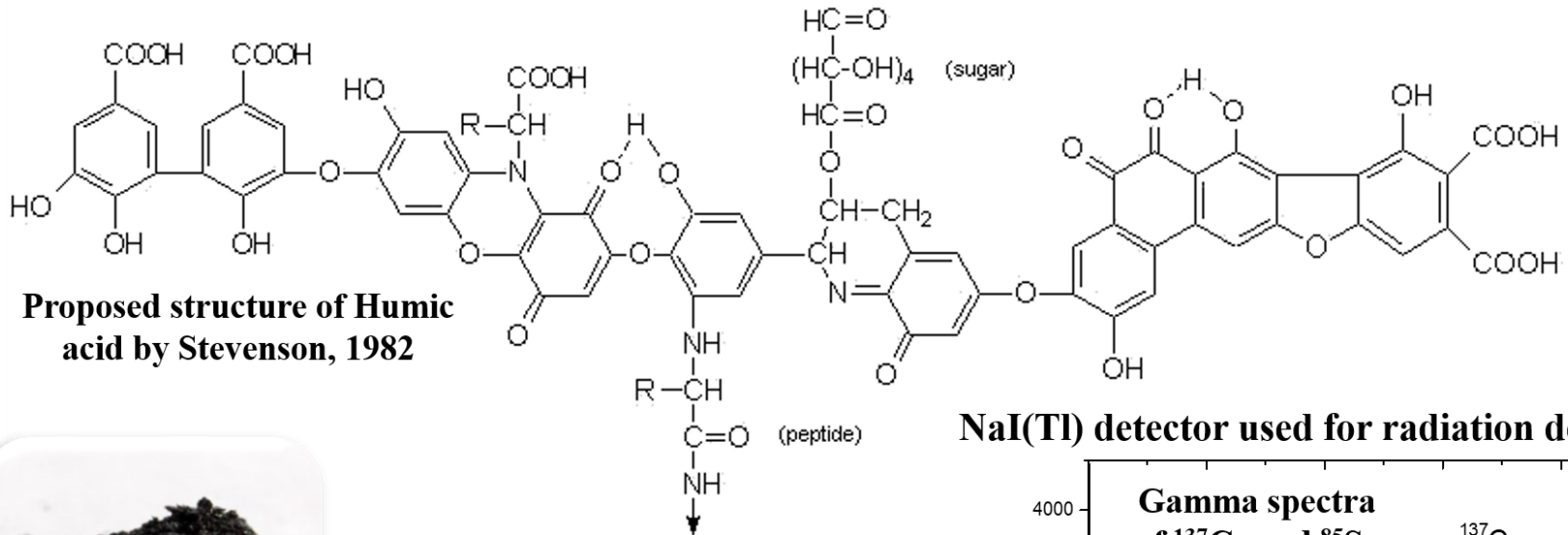
Rhexistasy

Periods of soil erosion

Soil Replenishing

HS/HA can be added to eroded and saline soils depleted in nutrients, to combat high saline stress and minimizes yield losses.

Methodology



Humic Acid

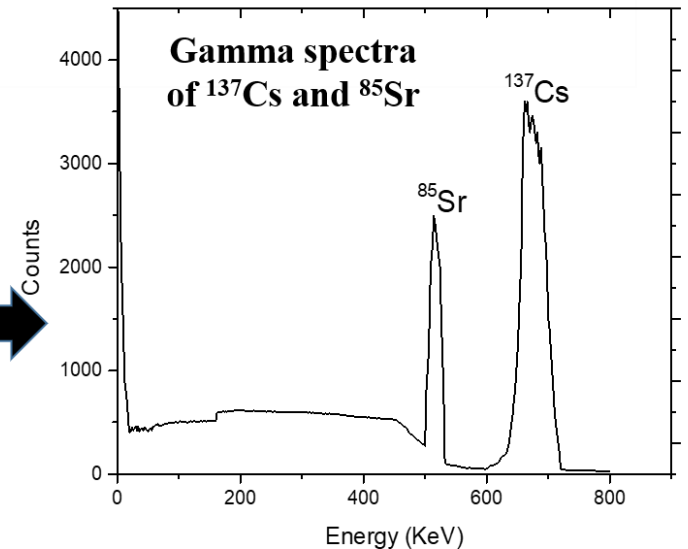
Polyfunctionality

Zwitterionic Character

Simulated low level radioactive waste solution comprising of:

- Cs(I), Sr(II), Co(II)
- NaI, NaNO₃
- Radiotracers ¹³⁷Cs, ⁸⁵Sr

NaI(Tl) detector used for radiation detection



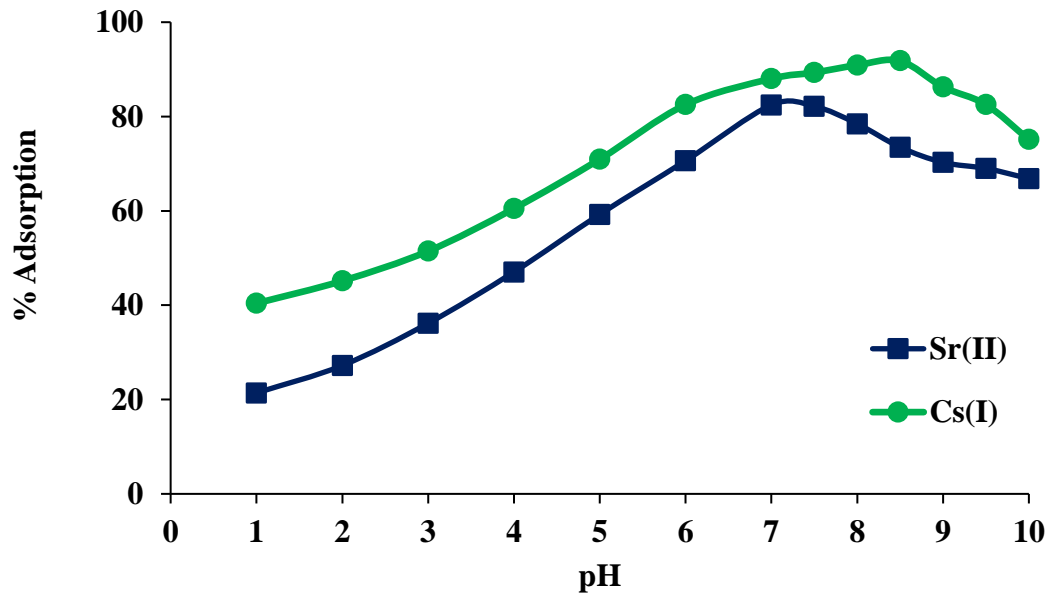
Biosorption of ^{137}Cs and ^{85}Sr : Experimental Parameters

pH

Amount

Time

Agitation



- Increase in pH leads to higher biosorption due to the protonated nature of the sorbent surface at low pH values, which causes repulsion between the sorbent and the metal ions in the acidic pH range.
- Biosorption drops at higher pH values owing to hydroxide formation

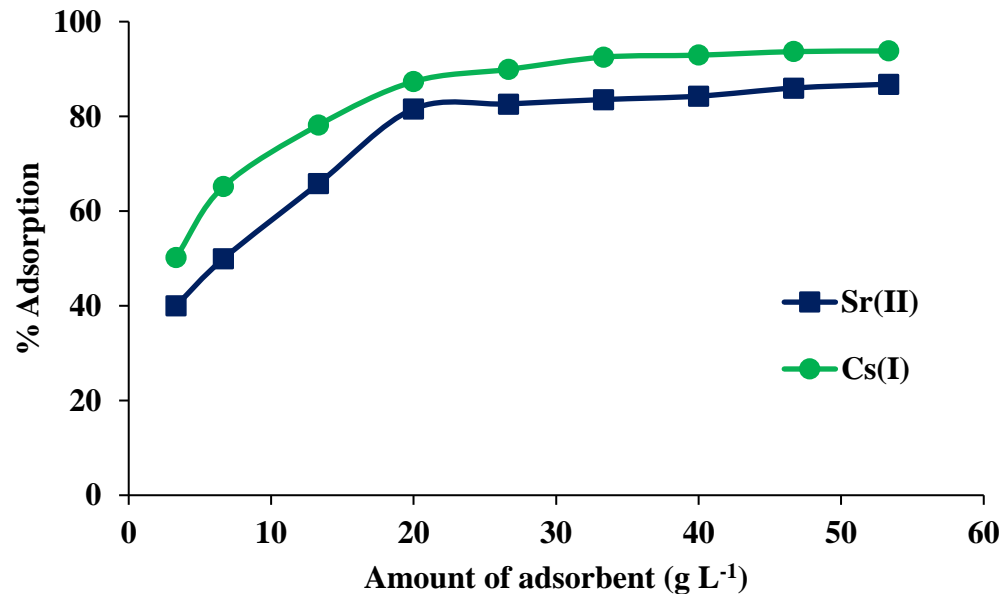
Biosorption of ^{137}Cs and ^{85}Sr : Experimental Parameters

pH

Amount

Time

Temperature



- Higher sorbent dose yields higher biosorption
- Upon further increase in sorbent dose, sorption attains a constant value, which may be attributed to partial aggregation of active sites present on the adsorbent.

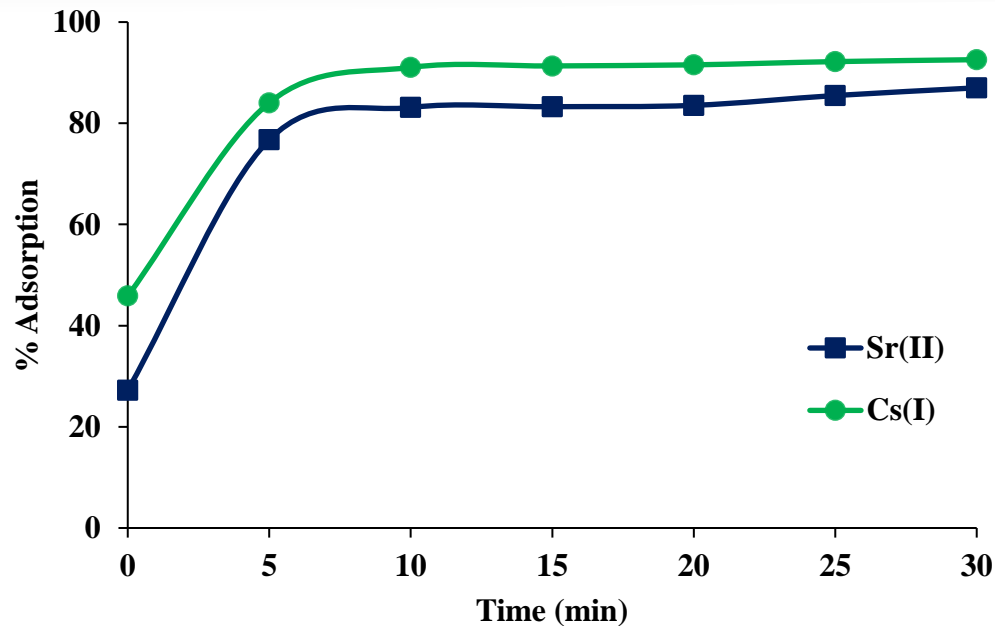
Biosorption of ^{137}Cs and ^{85}Sr : Experimental Parameters

pH

Amount

Time

Temperature



- As the contact time is increased from 0 to 30 min, adsorption of both the metallic ions rises and attains a maximum value at 10 minutes, beyond which there is no significant rise in sorption.

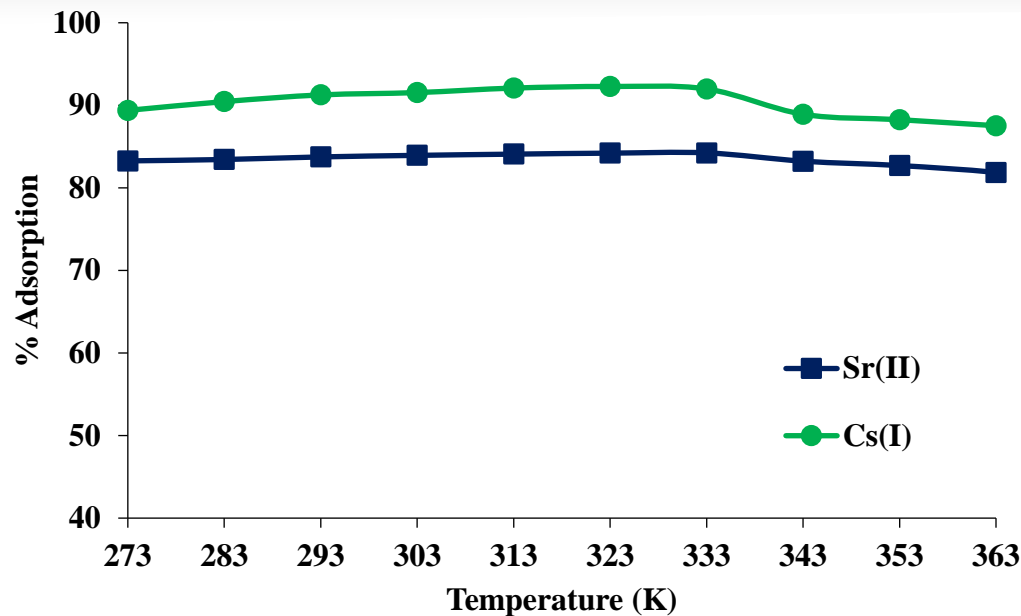
Biosorption of ^{137}Cs and ^{85}Sr : Experimental Parameters

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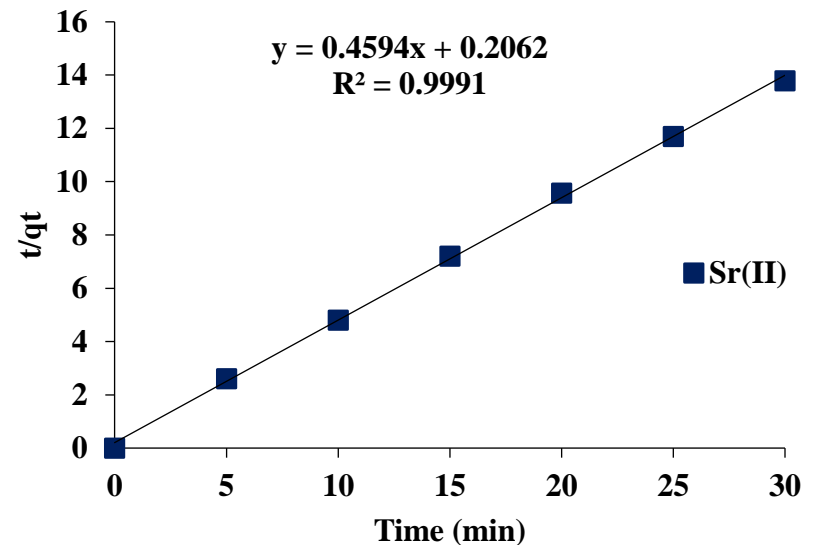
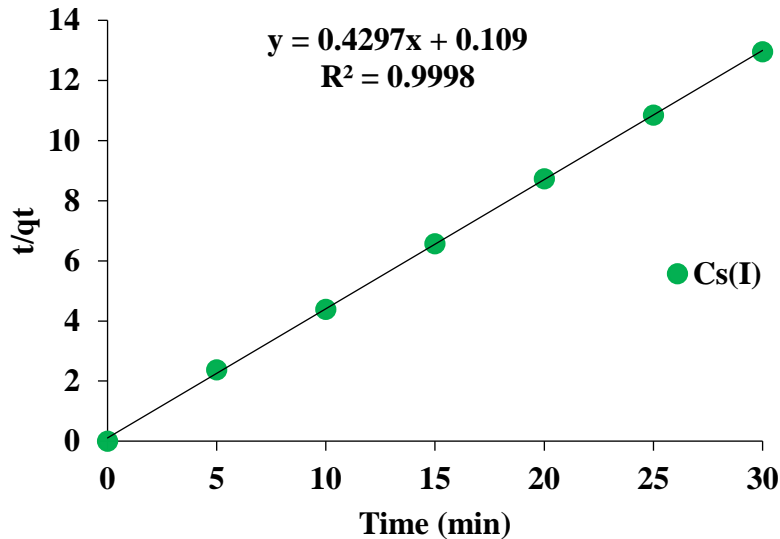
- It was noted that temperature has little effect on the biosorption of Cs(I) and Sr(II), which remains nearly constant up to 333 K.
- As temperatures exceed beyond 333 K, there is a gradual loss of sorbate ions.

Biosorption of ^{137}Cs and ^{85}Sr : Modelling Calculations

Kinetics

Thermodynamics

Pseudo Second Order Model by Ho & McKay



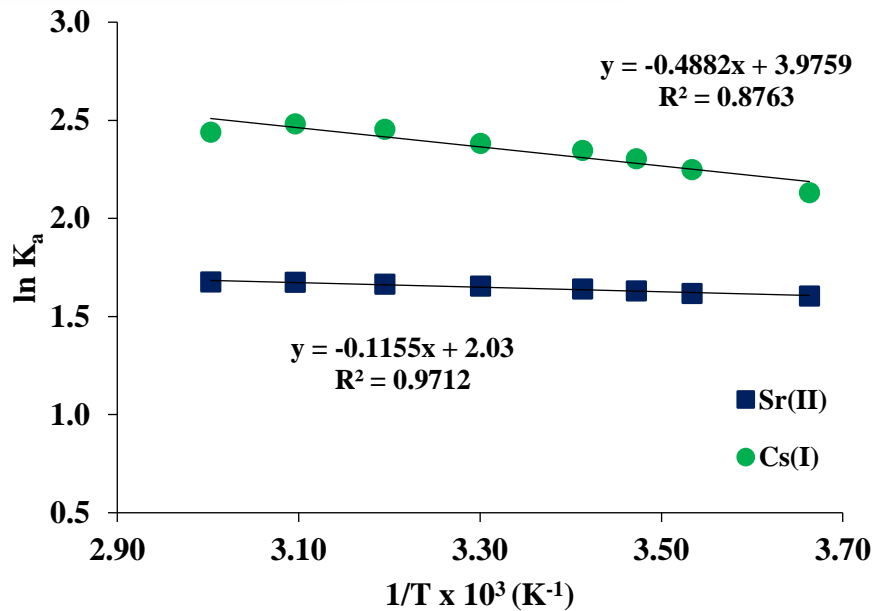
k_2 $\text{g.mg}^{-1}.\text{min}^{-1}$	q_e (Graph) mg.g^{-1}	q_e (Calc.) mg.g^{-1}	Interpretation
1.69	2.33	2.03	High R^2 and comparable q_e values prove applicability of this model which indicates chemisorption as the reaction mechanism

k_2 $\text{g.mg}^{-1}.\text{min}^{-1}$	q_e (Graph) mg.g^{-1}	q_e (Calc.) mg.g^{-1}	Interpretation
1.02	2.18	2.80	High R^2 and comparable q_e values prove applicability of this model which indicates chemisorption as the reaction mechanism

Biosorption of ^{137}Cs and ^{85}Sr : Modelling Calculations

Kinetics

Thermodynamics



Thermodynamic Parameters Obtained	Interpretation
Negative value of ΔG°	Spontaneous, Feasible
Negative value of ΔH°	Exothermic
Positive value of ΔS°	Strong interaction between sorbent and sorbate

Metallic Ion	$\Delta G^\circ = -RT \ln(K_a)$ kJ mol $^{-1}$	$\Delta H^\circ = \text{slope} \times R$ KJ mol $^{-1}$	$\Delta S^\circ = \text{intercept} \times R$ J mol $^{-1}$ K $^{-1}$	R^2
Cs(I)	-6.00	-4.06	33.06	0.8763
Sr(II)	-4.17	-0.96	16.88	0.9712

Conclusion: SWOC Analysis

STRENGTHS	WEAKNESSES	OPPORTUNITIES	CHALLENGES
<ul style="list-style-type: none">• Biosorption procedure is eco-friendly, economical and follows the principles of Green Chemistry.• Humic substances are naturally available organic matter.• Reaction time is particularly short as compared to other sorbents.	<ul style="list-style-type: none">• Structure of humic acid has yet not been elucidated completely	<ul style="list-style-type: none">• Owing to the presence of a variety of functional groups, HA scavenges a wide range of metal ions, hence can be used for wastewater remediation.• Selectivity of HA for Cs(I) and Sr(II) can be improved in the presence of salts.• Desorption studies	<ul style="list-style-type: none">• The study of interfering cations can be challenging due to chemical similarities of Cs(I) and Sr(II) with K(I) and Ca(II) respectively.

Conclusions

- The pH range of low level waste: 7.0-8.5, was found to be ideal for biosorption of ^{137}Cs and ^{85}Sr . This negates the need for addition of further chemicals, thereby making the process effectively, 'chemical-free'.
- $91\pm 2\%$ and $84\pm 1\%$ removal of radionuclides ^{137}Cs and ^{85}Sr respectively.
- High removal percentages and rapid kinetics, coupled with economic feasibility and benign nature of HA highlights the green nature of the process.

Optimized Experimental Parameters:

- ❖ pH: **7 to 8.5**
- ❖ Amount of HA: **20 g.L⁻¹**
- ❖ Contact Time: **10 mins**
- ❖ Temperature: **303 K**

Modelling Conclusions:

- ❖ Ho & McKay's Pseudo Second Order Kinetic Model – Chemisorption
- ❖ Thermodynamics – Spontaneous, Feasible and Exothermic reactions with positive entropy indicating affinity for the sorbent and sorbate

*Humic acid and its various forms thus act as **traps for radionuclides** and work as **excellent restorative soil stimulants** that supplement depleted soils, boost plant growth, and play a vital role in sustaining life on Earth.*