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Research paper



Biosorbents and Biosorption of Uranium Ions a Statistical Review

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Abstract

This study addresses the availability of various biosorbents and significance of characterization techniques used for biosorption of uranium ions. The improvements in nuclear technology have leads to increasing nuclear waste containing uranium being released and exposed in the surroundings.
The objective of this paper is to develop a better understanding the various techniques for the water system and environment were polluted with radionuclides (particularly uranium), considering the health effects of uranium, including varieties of biomasses and data of uranium uptake quantity at respective conditions, research issues concerning the biosorption process discussed. The accessibility of equilibrium models or adsorption isotherm is considering for fit the value for biosorption process. Moreover, it gives outlook of adherence and affinity of biomass towards the uranium ions particularly U(VI) was studied. This collective information in uranium adsorption biomasses at different pH and temperature used for U ions uptake. This paper shows the availability of organic living species and howfar it eliminates the toxic ions.

Keywords: *Biosorbent, Metal uptake, pH, Temperature, Uranium (VI)*

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1. Introduction

In this technological world, water is playing vital role for sustaining human life. Even though our planet has one-third of the earth surface to water. For drinking applications, the water availability is very low to the world population and the purity is needed with some good minerals. The climatic conditions done favor work for human by evaporating the ocean by cyclic process with help of sunlight. It is essential to prevent the contamination of heavy metal ions and intend to maintain the conditional parameters for existing water.
The health effects of excessive exposure to these heavy metals can be serious, especially for young and upcoming generation. It can cause delays in physical and mental development. Each year, large amounts of wastewater containing uranium are produced by the mining industry and industries that apply radioactive isotopes. The World Health Organization has determined that U (VI) is a human carcinogen and its concentration level in water should not exceed 50µg/L. The U.S. Environmental Protection Agency (1996) has recommended a drinking water standard of 20µg/L for ^{238}U. [1]. This study distinctly focus the view over biosorption, uranium health effects and various organisms used for uranium biosorption briefly to the limited extent.

1.1. Overview of Biosorption Process

Biological materials ability to heavy metals accumulation from wastewater through physical and chemical metal ions intake [2]. Biomass from algae, fungi, bacteria, sea-weeds and some higher plants, all of these have been effectively and successfully utilized in metal removal studies. Surfaces and interfaces define a boundary between a material and its surrounding environment and influence interactions with living and non-living biomass due to functional groups present in the cell walls exhibits attractive forces towards metal ions. [3].
In biosorption study there are three active fields of research.

(i) The elucidation of detailed sorption mechanism of metal ion onto the biomass surface.
(ii) The scaling up of the sorption process and its shifting from laboratory to field for its use to treat realistic effluents.
(iii) Search for an ideal biosorbent from an extensively large pool of available inexpensive biomaterials.

Due to commercialization of biosorption research projects, the above said points should consider in fact. There are several conventional methods for heavy metal removal from industrial effluents are Complexation, Co-ordination, Chelation, Cementation, Electro-winning, Electro-coagulation, Chemical precipitation, Lime coagulation, Ion exchange, Phytoremediation, Electrodialy-

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sis, Ultra filtration, Reverse osmosis and Solvent extraction [4]. Among these methods, biosorption is one of the processes with the use of biological materials, including living and non-living micro-organisms, in the removal and possibility to recovery of toxic metals from industrial wastes.

The major advantages of biosorption over conventional treatment methods include [5,6] are Low cost, high efficiency, minimization of chemical and biological sludge, no additional nutrient requirement, regeneration of biosorbent and possibility of metal recovery.

1.2. Basics of Uranium and its Toxicity

The selection of metals for biosorption studies is dependent on the angle of interest and the harmful degree of different metals, on the basis of which it is divided into four categories:

(i) Toxic heavy metals
(ii) Strategic metals
(iii) Precious metals and
(iv) Radio nuclides.

In terms of environmental threats, it is mainly categories (i) and (iv) that are of interest for removal from the environment and/or from point source effluent discharges.

Among these above said heavy metals, Uranium is highly toxic in many ways. So it is essential to study the biosorption of Uranium compounds so far. The degree of toxicity of Uranium mentioned briefly to the extent. Nowadays lots of uranium mines recognized and explored in many countries. The significance to use the naturally available biomass for adsorbing uranium compounds to keep the available natural resources safely to human culture.

Traces amounts of Uranium present in, soil rich areas, rock mountains, absorption over various plants and available with water resources. The natural source, radioactive and chemo toxic heavy metal Uranium was first coined by Martin Heinrich Klaproth in 1789. At that time who was a leading German chemist. After 100 years, Antoine Henri Becquerel discovered the radioactivity of uranium salts. In 1898 extracted for the first time 0.1 gram radium from 1000 kg of uranium ore In Paris. Marie Curie death due to leukemia in the age of 67 on 4th of July, 1934. Uranium is the fuel for nuclear reactors for generating electricity and a main raw material for nuclear weapons.

Generally Uranium had three isotopes: U-238, U-235, and U-234. Isotopes are atoms of the same element with the same number of protons, but a different number of neutrons, and thus different atomic weights. Uranium isotopes are radioactive (in Table 1)

Table 1: Some characteristics of uranium isotopes

Isotope	Proportion in natural U (%)	No. of Protons	No. of Neutrons	Half-Life (yr)
U-238	99.284	92	146	4.46 billion
U-235	0.711	92	143	704 million
U-234	0.0055	92	142	245,000

1.3. Migration of Uranium Mining and Processing Extracts in Environment "Uranium – Angel or Demon?"

Health effects of exposure to uranium can be a result of chemical and radiological toxicity of uranium. Uranium has long been known as a nephrotoxin and neurotoxin, which alters the normal activity of the nervous system and poisonous to the kidneys. Uranium targets particularly lungs and kidneys. The cautious thing caused by uranium is cancer. (Table 2). Uranium binds to biological molecules and follows calcium; it builds up in bone and teeth. Studies showed that the brain is also an affecting organ for uranium toxicity.

Notably mammals seem to have a high sensitivity to uranium. Once uranium is inside the organism, it is transferred to the extracellular fluids and transported through the blood to other organs. Uranyl, the soluble form of uranium, builds complexes with proteins and anions in the organism. Uranium can accumulate in the body and may have synergistic effects with other chemical and radioactive substances.

Uranium weakens the immune system and causes all sorts of health disorders including dermatitis and allergic reactions. More recently, uranium has been proven to mimic the effect of oestrogen at drinking water levels, which are considered as being "safe" by authorities. [8]. Uranium has a high affinity to DNA, which results in abnormally high absorption of natural background radiation and accelerates genotoxic effects [9]

This advanced biochemical and biophysical aspect of uranium contamination is described as "photoelectron enhancement effect".

Table 2: Uranium effects in human other than diseases of the respiratory tract [7]

Diseases	Collective
All solid cancers	U- workers
Benign and unspecified tumours	U-miners
Blood diseases	U-miners
Leukemia	U-miners Underground miners
Lymphoma	U-workers
Multiple Myeloma	U-miners
Gastric cancer	Underground miners and Population in U contaminated region
Liver cancer	U-miners Underground miners
Cancer of the gallbladder and extrahepatic bileducts	U-miners
Kidney cancer	U-workers
Mental disorders	U-miners

This means: uranium particles or uranium atoms bound to DNA amplify effects from external irradiation. Common dose-effect assumptions are therefore not sufficiently reliable to deny possible detriments by incorporated radioactivity. This is especially true for uranium miners and affected populations [9].

2. Characterization Studies and Summarization of Uranium Biosorption with Various Biosorbents

The swelling of emulsion increased with the concentration of carrier (tri-n-octylphosphine oxide), surfactant (sorbitan mono-oleate), internal phase and speed of agitation in Liquid Emulsion Membrane system. It was found that the absence of iron impurity, maximum recovery of Uranium obtained at these following parameters, (i.e.) internal phase concentration of sodium carbonate kept at 0.5M, extractant concentration at 0.005M, speed of agitation at 300 min^{-1} and pH of the feed phase around 3. [10]

The surface adsorption is a physicochemical phenomenon. The cell wall consists lipids, proteins, polysaccharides etc., and for that reason it's very essential to choose biosorbents (high affinity functional groups) to attracted heavy metals easily, otherwise treat with any preferred aqueous solutions. In some biosorbents naturally the functional groups in-built in the cell walls offer a host of functional groups capable of binding to heavy metals.

The amino, carboxylic, sulfhydryl, phosphate, and thiol functional groups differ in their affinity and specificity for metal adherence. The surface-bound metal ion is then transported into the cytoplasm through the diffusion barrier presented by the cell membrane. Since a fixed cell biomass offers a finite number of surface binding sites, the initial uptake, being surface adsorption, would

be expected to show saturation kinetics with increasing metal ion concentration. [11]

Table 5: Regeneration of Bisorbents [11]

S.No	Biosorbents	Recovery % of uranium ions
1	Carboxymethylcellulose	98
Dried powdered fungal mycelia		
2	Trametes versicolor	91.8
3	Phanerochaete chrysosporium	66.8

The uranium extraction from integrated nuclear desalination systems had been removed by using three innovative and effective methods are proposed. The various recovery methods of uranium like ion exchange, solvent extraction, foam separation, co-precipitation, biological separation, usage of adsorbents like TiO_2, activated carbon, Galena using of polymers as adsorbents like hydroxamic acid chelating polymers, methacryloyl amido-glutamic acid polymer and uranium recovery using amidoxime polymer had some comparatively low advantages .So the author proposed innovative or improved methods of uranium extractions are (i) Resin grafted with calixarene (ii) Magnetic separations (iii) Canal system with Braid adsorbents.[12]

Citrobacter freudii, a bacterial type biosorbent to adsorb uranium ions. In this study, author investigated the active sites like carboxyl groups present in the cell wall played vital role of bacteria by SEM analysis. [1] Citrobacter freudii was proven to be an excellent biosorbent for uranium adsorption. Scanning Electron Microscope (SEM) observation was discovered the morphological change of biomass before and after adsorption. Since dead bacteria have better adsorption performance than live ones, the chemical groups upon the cell walls rather than biological activity were responsible for biosorption. The pretreatment of bacteria culture using NaOH and methanol-thick hydrochloric acid, the carboxyl on the cell walls was locked as one of the active sites of adsorption.

The morphology of the biomass was observed by SEM, the surface of bacteria before adsorption was slippery, clean and it had been observed that after adsorption its became abnormal and a great deal of crystal adhered to the surface. The same observation noticed for biosorbents named as Rhizopus arrihizus. [13]

The role of Pseudomonas strain and its characterization is briefly studied. The author employed the chemical nature of bacteria–radionuclide interaction in this paper. Intracellular radionuclide (uranium and thorium) deposition is observed through the following equipments such as (i) Transmission Electron Microscopy exposes the presence of electron dense micro- precipitation of deposited metals. Elemental analysis of biomass and uptake solution indicated that uranium and thorium binding by the bacterial cells is possibly mediated by displacement of cellular potassium and calcium ions. (ii)Involvement of cellular phosphate, carboxyl and amide groups in uranium and thorium binding is evident from FTIR spectroscopy.

(iii)Role of cellular phosphate groups in uranium and thorium sequestration is confirmed by X-ray powder diffraction analyses that showed deposition of crystalline uranium within the cell biomass.

(iv) Atomic force microscopy showed enlargement of bacterial cells following radionuclide sorption along with increase in surface roughness. The author affirms using characterization tests, the test implies a combined methods are ion-exchange–complexation–micro precipitation mechanism. [14]

S.No	Organisms as Biosorbent	Operating Conditions		
		pH	Temp (˚C)	Uptake (mg/g)
1	Myxococcus Xanthus (Bacteria) [15]	4.5	28	2.4mM/g
2	Immobilized and powdered dry biomass [11] Trametes versicolor	4.5	20	309.1
	Phanerochaete chrysosporium	4.5	20	158.01
3	Microcystis aeruginosa [16] (Cyanobacterium bloom)	4 8	30 30	48 44
4	Lentinus sajor-caju (Fungus) [17] Alkali(NaOH) treated Alkali untreated Heat treated	 4.5 4.5 4.5	 25 25 25	 378 268 342
5	Catenella repens (Red alga) [18]	4.5	30	303
6	Citrobacter freudii (Bacteria) [1]	5	55	48.02
7	Pseudomonas putida (Bacteria) [19] Dead cell Lived cell	 6 6	 30 30	 2.91 0.53
8	Starfish(Dried) [19]	6	30	1.14
9	Rhodotorula glutinis (Chemically modified) [20]	6	25	149
10	Aspergillus fumigates (Immobilized beads) [21]	5	30	200 mg/L
11	Rhizopus arrihizus [22]	4	30	112.2
12	Cystoseira indica alga(Ca-pretreated) [23]	4	45	318.15
13	Cystoseria indica(algae) [24]	4	15	233
14	Bi-functionalized biocomposite adsorbent Jania rubens (macro marine algae) and Saccharomyces cerevisiae (yeast)) [25]	4	30	43.2
15	Chitosan/clinoptilolite [26]	4	20	536.35
16	Penicillium citrinum (dead fungal biomass) [27]	6	45	274.73
17	Aspergillus niger powder beads[28]	5	30	649.4
18	Tea Waste[29]	6	30	142.21
19	Saccharomyces cerevisiae (onto cross-linked chitosan coated) [30]	4	30	72.4
20	Pummelo Peel[32]	5.5	30	270.71
21	Deinococcus radiodurans cells [33]	4	25	230
22	Wheat straw[34]	3	30	1.20
23	Bacillus mucilaginosus [35]	5.5	35	172
24	Palm Shell Powder (PSP) [36] Acid treated palm shell powder (APSP) Steam treated palm shell powder (SAPSP) Persulfate treated palm shell powder (PAPSP) Acid activated carbon (9AAC) Modified Palm shell powder (MPSP)	 1 	 30 30 30 30 30 30	 249.4 253.8 252.5 232.6 244.5 235.9
25	Pleurotus mutilus (Fungal biomass) [37]	2	15	636.9
26	Chitin-based marine sponges[38]	7	25	288
27	(i)Rice Straw activated carbon(modified with KOH) [39] (ii)Humic acids	5.5 5.5	25 25	100 21.1
28	Banyan Leaves [40]	3	35	22.06
29	Eucalyptus citriodora distillation sludge [41] Eucalyptus citriodora	4 4	30 30	57.75 83.25

	distillation sludge treated with Benzene			
30	Fusarium sp. #ZZF51, mangrove endophytic fungus [42] (i)Raw biomass (ii)chemically modified by formaldehyde, (iii)chemically modified by methanol (iv)chemically modified by acetic acid	 6 6 6 6	 30 30 30 30	 318.04 311.95 351.67 21.42
31	Chlamydomonas reinhardtii [43] Free algal cells Entrapped algal cells Bare CMC beads	 4.5 4.5 4.5	 25 25 25	 337.2 196.8 153.4
32	Coconut Husk Activated Carbon[44]	6	25	6.67
33	Trapa bispinosa[45]	5	50	171
34	(Cochlospermum gossypium) Gum Kondagogu - natural biopolymer[46]	4	25	487
35	Pollen pini (Pinus massoniana pollen)[47]	2.5 5	25 25	170.648 448.430
36	(i) Cetyltrimethyl ammonium bromide treated Fusarium sp. #ZZF51 (CTAB-treated biomass) [48] (ii) Native Biomass	7 7	30 30	400.10 21.42
37	Novel Streptomyces sporoverrucosus dwc-3[49]	3	30	3
38	Eichhornia crassipes [50]	5.5	30	142.85
39	Cyclosorus interruptus (CI) [51] Raw-CI, Ca-CI, Mg-CI Mg/H2O2-CI	 5.5 5.5 5.5 5.5	 20 20 20 20	 41.67 52.63 62.50 71.43
40	Cladophora hutchinsiae (green algae) [52]	5	20	152
41	Vigna radiata [53]	4	40	230
42	Bacillus vallismortis [54]	4 - 5	35	23.6
43	Bacillus subtilis / Fe3O4 [55]	4	60	25.03
44	Novel Luffa cylindrica (LC) adsorbent modified with polyethyleneimine (PEI) "grafting-from" approach (LC-EPI-PEI) "grafting-to" approach (LC-PGMA-PEI) [56]	6 6	25 25	208.3 438.5

The infrared (IR) spectra of raw, chemically modified and uranium bounded Rhodotorula
glutinis cells were obtained using Fourier transform infrared spectrometer. Sample dicks were made by mixing 5 mg of dry biomass with 150 mg of KBr and pressed them into tablet form. All infrared spectra were recorded over 4000-400 cm^{-1} region with a resolution of 0.2 cm^{-1}. [20]

Table 4: Characterisation of Rhodotorula glutinis biosorption and FTIR spectrum analysis [20]

S.No	Description	Vibrational modes	Wavenumber(cm-1)	Functional groups
1	Raw Biomass	Stretching	1065	Carboxyl (C-O)
2	Raw Biomass	Stretching	3289-3303	Amino and Hydroxyl group
3	Biomass-Methanol	Stretching	1732	Ester carbonyl
4	Biomass-Methanol	Stretching	1076	Esterification of Carboxyl group
5	Treated and untreated biomass (After Biosorption)	Asymmetric Stretching	905-916	Uranium Ions (UO_2^{2+})

Scanning electron microscope indicates the presence of pores had large surface area and rough structure in the bio-composite adsorbent. The size of the pores measured using SEM approximately 5µm which was more sufficient to enhance biosorption of uranium ions from aqueous solutions and uranium complexes. [25]
In this study, the FT-IR spectra of biocomposite adsorbent showed the presence of many functional groups. The biosorption property of U (VI) by bi-functionalized biocomposite adsorbent consists of macro marine algae (Jania rubens) and yeast (Saccharomyces cerevisiae) immobilized on silica gel. The characteristics peak 3461.66 cm^{-1} due to stretching of the O-H group in biocomposite. This N-H stretching peak lies in the spectrum region occupied by a broad and strong band (3200–3600 cm^{-1}), which is due to the presence of γ O-H of the hydroxyl groups 2300–2400 cm^{-1} region is because of NH_2+, NH^+ and N-H bond of biocomposite. All three spectra for the biocomposite adsorbent revealed the presence of protein related bands. Absorption peaks in between 1000 and 1100 cm^{-1} assured the presence of carboxyl groups in the polysaccharide structure. Strong absorbance in that peak at 1648 cm^{-1} is shows the three helical structure of proteins and also amino sugars. The role and ability of non-living biomass of Penicillium citrinum has been explored and FTIR spectra are discussed in Table 6.
This reveals that these functional groups such as –OH, –NH, and COO− are available for interaction with uranium ions.

Table 6: Characterisation of Penicillium citrinum biosorption and FTIR spectrum analysis [31]

S.No	Description	Vibrational modes	Wavenumber(cm^{-1})	Functional groups
1	Raw Biomass	Stretching	3289	Hydroxyl group (–OH)
			3399	Amino group(–NH)
			1384	C(=O)–O−
2	Biomass (After Biosorption)	Stretching	918	Uranium Ions (UO_2^{2+})

3. Scope and Future Directions

Further literature works in the following area is needed to be carried out in order to establish the viability of uranium extraction and its characterization studies due to its essential. For the past three years the research fail to study the desorption methods and hygienic disposal of harm ions.

1) Study of kinetics model of uranium is required to choose optimum conditions as it passes through the various stages of the beds, columns and different methodologies. Specially the effect of temperature, several functional groups presents in biosorbents, pH and the effect of added chemicals etc., must be studied and known before choosing a correct extraction technique.
2) However the water has been more important and next to that definitely electricity had the responsibility to run the modern world. The requirements of uranium had increased due to nuclear power generation for electricity production.
3) The world waiting for unpolluted nature and this review of papers explained the availability of enormous segregation methodologies and various essential hazardous elements us-

ing several biosorbents have been awaited for commercialization.

4) The most questions in adsorption, the disposal of the heavy metal for further studies are needed recovery.

4. Conclusion

The results of present studies showed that Uranium ions could be effectively adsorbed by various biomasses. It also shows adsorption capacity of Uranium decreased with the increase of biosorbent dose. The percentage removal of uranium ions increased with the increase of initial uranium concentration. The temperature, pH, and functional groups present in the biosorbents mostly responsible for the alteration sorption mechanism. Since the reaction order of biosorption process cannot be theoretically predicted, it is not necessary to preset the order of biosorption kinetics to be the first or second as commonly exercised in biosorption studies. The time taken for the adsorption equilibrium and initial concentration, a factor affecting adsorption constants in the various kinetics models to analyze. This study mainly shows the characteristics of active sites present in various biosorbents and the affinity towards the uranium ions.

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