**Review Article**

# Sorption of Radionuclides

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## ABSTRACT

Chitin, chitosan, chitin- and chitosan- derivatives, living and dead fungi, and modified fungal biomass have been used for their ability to sorb metals, radionuclides, dyes and ions from water, waste water, soil and other contaminated sources. These sorbents are based on chitin, contain a large number of functional groups such as hydroxyl and amino groups enabling them to exhibit high sorption potential. Chitin and related-derivatives owing to their low cost, high sorption capacities, ease of use and ability to regenerate have found significant acceptance for removal of radioactive pollutants. Biosorption using fungi has been achieved with surprising success. This review includes fungi from divisions of Ascomycota, Basidiomycota and Zygomycota due to the presence of chitin and chitosan as significant components of their cell walls. In this review, an extensive list of chitin, chitosan, chitin- and chitosan- derivatives, living and dead fungi, and modified fungal biomass from vast literature was reviewed and their sorption capacities for a variety of radionuclides as available are shown.

**Keywords:** Chitin, Chitosan, Radionuclides, Adsorption.

## INTRODUCTION

The recovery or removal of radionuclides from sea waters and waste waters is a challenging problem. According to the fundamental principles of radioactive waste management, radionuclide waste minimization is required to be done in an effective manner. The principal sources of radionuclides are soil, rocks, sea water and tailings of mineral processing activities. Increase in the amount of radionuclides in the environment has occurred due to a number of anthropological activities like mining, benefaction of radionuclides from their ores, processes related to nuclear power plants and the manufacture of atomic weapons, and use of radionuclides in medical diagnosis and treatment techniques. These applications of radionuclides produce various solid and liquid wastes containing a cocktail of different isotopes. These wastes are known to cause intense toxicological impacts and destructive illnesses for human[1]. Table 2 gives the activities and health effects of some radionuclides. Hence, United State Environmental Protection Agency (USEPA) and World Health Organization (WHO) have directed maximum concentration level of uranium in drinking water to be 0.030 and 0.015 mg/L, respectively (WHO, 2004).

The new advanced treatments for the removal of these hazardous materials has reached its endeavours recently. The most commonly used methods for the removal and recovery of radionuclides includes adsorption, membrane filtration, solvent extraction, reductive precipitation, bio-precipitation, biosorption, dialysis, chromatography, and ion exchange methods[2,3]. Among these different techniques, adsorption is the economically feasible technique and it has been developed as the guaranteed procedure for water and wastewater treatment.

The use of natural polymers as adsorbents has gone through a new shift, especially polysacchrides like chitin and its derivative chitosan. Henrni Braconnot, a French Professor first discovered chitin in mushrooms, in 1811. Later in 1820s chitin was also isolated from insects[4]. Chitin contains 2-(acetylamino)-2-deoxy-D-glucose units connected via β-1, 4 linkages. Chitin is the second most abundant polymer in nature after cellulose. It can be extracted from crustacean shell such as prawns, crabs, fungi, insects and other crustaceans.

Some sources of chitin and source organisms have been shown in Table 1. Chitin (Fig. 1a) is depicted as cellulose with one hydroxyl group on each monomer replaced with an acetyl amine group. This increases hydrogen bonding between nearby polymers, providing the chitin-polymer matrix greater strength.

Chitosan was discovered in 1859 by Professor C. Rouget. Chitosan (Fig. 1b) is composed of randomly distributed β-(1-4)-linked D-glucosamine and N-acetyl-D-glucosamine. It is prepared by treating shrimp and other crustacean shells with alkali sodium hydroxide[4].

Chitosan can be used as an adsorbent to remove radionuclides due to the presence of amino and hydroxyl groups, which serve as the active sites. This biopolymer represents an appealing alternative to other biomaterials on account of its physico-chemical characteristics, chemical stability, high reactivity, magnificent chelation behaviour and high selectivity towards pollutants. Chitosan has been modified by several methods either physical or chemical to enhance its physical properties to achieve greater adsorption capacity for different radionuclides. Different shapes of chitin and related-derivatives such as beads, hydrogels, membranes, films, resins and microspheres have been examined for their adsorption efficiency of various pollutants.

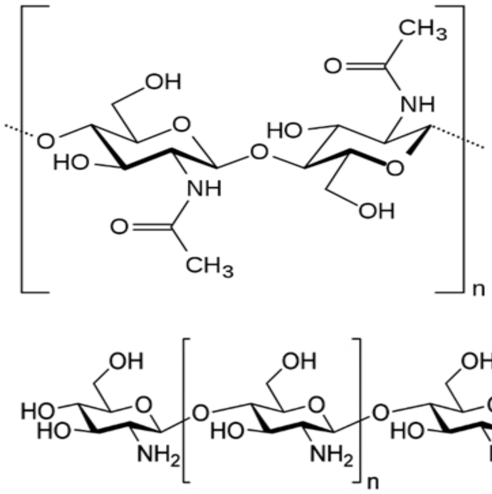

**Figure 1: a)** Chitin; **b)** Chitosan

In the present work, the aim is to review of the adsorption potential (adsorption capacities) of chitin and related-derivatives for various radionuclides e.g. uranium, thorium, americium, cesium, technetium, etc.

**Table 1:** Some radionuclides along with their activities and health effects.

| Radionuclides | Activity | Health Effects |
|---|---|---|
| Uranium-238 | 3.3 × $10^{-7}$ Ci/g | Heavy damage to kidney |
| Thorium-232 | 1.1 x $10^{-7}$ Ci/g | Tumours and Leukaemia |
| Strontium-90 | 1.5 x $10^{2}$ Ci/g | Bone cancer |
| Uranium-233 | 9.5 x$10^{-3}$ Ci/g | Renal and CNS damage |
| Thorium-234 | 2.3 x $10^{4}$ Ci/g | Lung and pancreatic cancer |
| Cesium-137 | 8.8 x $10^{1}$ Ci/g | Cancer and burns |
| Europium-152 | 1.9 x $10^{2}$ Ci/g | Cancer |
| Americium-241 | 3.2 Ci/g | Cancer |
| Strontium-85 | 2.4 x $10^{4}$ Ci/g | Bone cancer |
| Strontium-89 | 2.9 x $10^{4}$ Ci/g | Cancer, Affects foetus in pregnant women |
| Cobalt-60 | 1.1 x $10^{3}$ Ci/g | High risk of cancer |
| Manganese-54 | 8.3 x $10^{-3}$ Ci/g | Cancer |
| Cerium-141 | 2.8 x $10^{4}$ Ci/g | Cardiovascular collapse |
| Technetium-99 | 1.7 x $10^{-2}$ Ci/g | Soil pollution and degradation |
| Iodine-129 | 1.6 x $10^{-4}$ Ci/g | Affects thyroid |
| Europium-154 | 1.5 x $10^{2}$ Ci/g | Cancer |
| Nickel-63 | 4.6 x 10 Ci/g | Cancer |
| Radium-226 | 3.7 x $10^{10}$ Ci/g | Lymphoma, bone cancer |

**Table 2:** Sources of chitin and the source organisms.

| Source of Chitin | Some source organisms |
|---|---|
| Cell walls of fungi | Higher basidiomycetes |
| Exoskeletons of arthropods (crustaceans & insects) | Crustaceans: crabs lobsters and shrimps<br>Insects: Beetle |
| Radulae of molluscs | Cuttlefish, snails and slugs |
| Internal shells of cephalopods | Bigfin reef squid |
| Squids | - |
| Octopus | - |

## Chitin- and Chitosan- Derivatives for Radionuclides Removal

Radionuclides are a very significant category of environmental pollutants that can harm human health as well as impact other terrestrial and aquatic organisms. Chitin- and chitosan-derivatives can be regarded to their unique properties such as high hydrophobicity, presence of many functional groups, flexible structure and high chemical reactivity.

### Natural Chitin and Chitosan

Shrimp shells is one of the major sources of chitin. Chitin extracted from decalcified shrimp shells has been used to investigate the ability to adsorb uranium from solutions[5]. An absorption capacity of 7.484mg/g was observed at optimum conditions. Langmuir isotherm model was followed. The kinetic modeling data indicates the rate of sorption to follow pseudo second-order. The mechanism of uranium adsorption by chitin involves 3 steps: a) interaction between uranium ions and the chitin chain; b) adsorption of uranium ions by chitin network; and c) hydrolysis of the formed complex followed by precipitation of hydrolyzed compound[6,7].

Removal of technetium-99 ($^{99}$Tc), iodine-129 ($^{129}$I), and cesium-137 ($^{137}$Cs) from contaminated ground water and sediments using Chitosan was investigated[8]. The sorption of Cs on sediments is stronger compared to Tc and I as corroborated by the $K_d$ value which is quite high for Cs.

Coprecipitation efficacy of $^{233}$U, $^{239}$Pu, $^{241}$Am, $^{152}$Eu, $^{90}$Sr, $^{90}$Y, and $^{60}$Co by low-molecular-weight chitosan (LMWC, MW=5 kDa) and high-molecular-weight chitosan (HMWC, MW=700 kDa) was investigated[9]. Experiments showed LMWC to be a more effective coprecipitant than HMWC. LMWC was synthesized from HMWC via enzymatic action of *S. Kurssanovii* [10]. Using HMWC, the degree of coprecipitation (α) was found to be 99% for $^{233}$U and $^{241}$Am, 80% for $^{152}$Eu and $^{90}$Y, and 85% for $^{239}$Pu.

Chitosan granules and nanofibres were prepared for sorption of $^{238}$U and $^{137}$Cs [11]. It was found that U(VI) sorption on bare granules (chitogran- C) and those cross-linked by glutaraldehyde (chitogran-Cs) ocurred by external diffusion whereas for freshly formed granules (chitogran-M) sorption occurred due to internal diffusion. Cross-linking resulted in increased strength and stability for the chitogran in acidic solutions but reduced sorbent capacity. Cs sorption remained unaffected in presence of competing ions. Recovery of chitogran was achieved with elution by 0.02 M sulfuric acid and 0.6 M ammonium bicarbonate for Cs and U respectively. Nanofibrous chitosan containing materials provided quicker sorption and more extraction. The sorption associated with Nickel on chitosan was investigated[12]. Being a tracer was employed radioisotope $^{63}$Ni. The influence of contact time, effect of pH and effect of foreign ions on sorption of nickel on chitosan was studied. The percentage of nickel sorption on chitosan in the observed initial pH ranging was 97 %.

## Magnetite containing products

Chitosan impregnated with magnetite nanoparticles was synthesized to examine the removal of uranium ions from water and sodium carbonate solution showed a desorption efficiency of 94 %[13]. A novel adsorbent was prepared in the form of magnetic chitosan beads for the removal of $Sr^{2+}$[14]. The kinetic data correlated the adsorption process by intra particle diffusion model. The FTIR study revealed that $-NH_2$majorly took part in the sorption of $Sr^2$ by magnetic chitosan beads.

With the help of an in-situ process, novel magnetic chitosan composite particles of average size 40μm and saturation magnetization of 24 emu/g were prepared and evaluated for decontamination of radioactive waste water[15]. Sorbent characterization by SEM, EDX, FTIR and magnetization measurements was done which showed that the target ions were bound and their surface distribution was uniform. The composite under study was found to have higher adsorption for uranyl (666.67 mg/g) and thorium (312.50 mg/g) ions. Repeated adsorption and desorption cycles showed that the material may be regenerated and reused.

An amine bearing chitosan was reported by Elwakeel for the sorption of uranium[16]. SEM analysis of TEPA@MCHS beads after U(VI) adsorption showed a smooth surface with small particles on surface, instead of the multi-microporous, rough surface with appended pores before adsorption. Elution of the uranium ion loaded resin with 0.5 M Hydrochloric acid was found to reach 98% desorption.

## Imprinted Chitosan

Chitosan modified via metal ion imprinting (MIP) technique has been prepared to selectively uptake Co(II) from solutions[17]. MIP chitosan was found to have maximum sorption compared to NIP (Non-Imprinted) chitosan in citrate solution. MIP showed selectivity for Co(II) in presence of competing Fe(II) while NIP showed similar sorption capacities for both. Sorption of Co(II) by MIP from NAC formulations that are strongly complexing displays its use in the preferential sorption of Co(II) from complexing solutions. Elution with 0.25 M sulphuric acid solution in batch process gave nearly 100% desorption was achieved in 1 hr.

Application of surface ion-imprinting concept and sol–gel process in preparation attapulgite-supported-chitosan polymer for the selective adsorption of Ce(III) from aqueous solution was studied[18]. The optimum pH was observed to be 4.0, during which the mass of Ce(III)-MIPs was over 0.12 g and quiescent time was over 15 min. The adsorption rate towards Ce(III) nearly reached to 100%. Ce(III)-MIPs have well regenerative capacity which was evident from the adsorption capacity of Ce(III)-MIPs after four regenerations that slightly decreased.

## Composite Products

A novel adsorbent poly(methacrylic corrosive)-joined chitosan/bentonite (CTS-g-PMAA/Bent) composite was synthesized for uranium (VI) adsorption[19]. The process followed Langmuir isotherm model. It was also found that CTS-g-PMAA/Bent was mechanically and chemically robust for the recovery of U (VI) from aqueous media as well as industrial waste.

Poly(methacrylic acid) – grafted composite/bentonite, a novel composite matrix, was prepared. Batch experiments were conducted to study the extent of Th(IV) adsorption[20]. The adsorption capacity of PMAA-g-CTS/B was found to be 99.8%. Repeated adsorption–desorption experiments showed that PMAA-g-CTS/B (the adsorbent) had a high potential for the removal and recovery of Th(IV) from aqueous media.

A novel chitosan/clinoptilolite (CS/CPL) composite was used for adsorption of $UO_2^{2+}$ and $Th^{4+}$ ions from radioactive solutions[21]. The adsorption process was spontaneous ($\Delta G^{\circ} < 0$) and endothermic ($\Delta H^{\circ} > 0$). The results obtained in the desorption process indicated 0.1M $Na_2CO_3$ as the best desorption agent for the $UO_2^2$ ions, while for the desorption of the $Th^{4+}$ ions, the best results were obtained with 0.1M HCl solution thereby indicating the reusability of the adsorbent.

## Cross-linked Chitosan Products

Two chitosan derivatives: cross-linked chitosan (CRC) and cross-linked chitosan after hydrolysis (CRCH) were prepared for extraction of $^{137}$Cs, $^{85,89}$Sr, $^{152}$Eu, $^{241}$Am, $^{234}$Th and $^{233}$U using batch and column methods[22]. The $\tau_{1/2}$ (Half-life) for U appeared to be in the range 120-150 minutes for CRC and CRCH. For other metal ions, the $\tau_{1/2}$ was found to be in the range from 240 – 254 min. The ion uptake trend was as follows: $UO_2^{2+}$> $Th^{4+}$> $Cs^{+}$> $Eu^{3+}$> $Am^{3+}$> $Sr^{2+}$ and the $K_d$ value was found to decrease with increasing acidity. CRCH has a higher uptake capacity compared to CRC. However, CRC showed greater selectivity for uranium due to the presence of nitrogen donors for selective binding. Elution of uranium loaded on CRCH with disodium carbonate gave 97% recovery and more than 95% elution of Th was obtained with EDTA.

## Modified Chitin and Chitosan Products

Adsorption of Uranium (VI) from aqueous solution onto modified chitosan, i.e., chitosan grafted with citric acid was investigated[23]. Kinetic studies showed that the adsorption rate was determined by interfacial boundary diffusion mechanism. The adsorption capacity was found to be 24 mg/g. Elution with 0.1 M $NaHCO_3$ solution giving a maximum recovery of 99.78%.

Sorption of $^{90}$Sr, $^{90}$Y, $^{137}$Cs, and $^{233}$U on newly synthesized derivatives of HMWC and LMWC was examined[24]. The following derivatives were synthesized Succinyl chitosan Na salt (SHMWC), Succinyl chitosan Na salt (SLMWC) N-(2-Hydroxybenzyl) chitosan (HBHMWC), Chitosan cross-linked with 2-{2-[2-(2-formylphenoxy)ethoxy]ethoxy} benzaldehyde (LMWCDA), N,O-(2-Hydroxy-2-N,N-dicarboxymethyl)ethyl chitosan (IDA-HMWC), and N-(3-Sulfo-3-carboxy)propionyl chitosan (N-SSLMWC). Of all the derivatives, SLMWC and N-SSLMWC were found to be soluble in solution at pH range 1 – 10. $^{90}$Sr did not sorb effectively on any functional derivative.

To improve the adsorption properties of chitin it was modified with dithizone for adsorption of $^{60}$Co[25]. Natural and dithizone-modified chitin was characterized using surface area analyzer and infrared spectroscopy. Dithizone-modified chitin was found to have a greater surface area than natural chitin. Adsorption of $^{60}$Co was found to increase with pH on dithizone-modified chitin. At low pH, protonation of active sites prevented adsorption. The equilibrium time was found to be 180 minutes at which the adsorption reached 60 and 96% for Ch and Di-Ch, respectively. The process is spontaneous and exothermic, due to a positive enthalpy value.

## Other Derivatives

Multiwall Carbon Nanotubes were used and modified to be used with chitosan for U(VI) adsorption[26]. The removal of U(VI) by MWCNTs and MWCNT-CS increased with raising pH values at pH<7, and then decreased together with raising pH values at pH>7.

The final results suggest that MWCNT-CS can be employed for U(VI) preconcentration and other lanthanides/actinides. Adsorption actions associated with Sr(II) ions was reported using carboxymethylated chitosan (CMCts)[27].

The adsorption of Sr(II) ions discloses that minimizing pH as well as improving ionic strength can reduce the actual adsorption ability of Sr(II) ions.

The advantage of using chitosan cryogel modified with pyridoxal-5´-phosphate for extraction of $^{152,154}$Eu(III) from aqueous solutions was examined[28]. The chitosan cryogels have an ultramacroporous structure with pores of diameter range from 50-100 μm. Modification of chitosan cryogel with pyridoxal-5´-phosphate improved the sorption properties with respect to Eu(III).

A new inorganic ion-exchanger into biopolymer foams combination biosorbent was prepared by immobilization of Nickel–potassium ferrocyanide in highly porous discs of chitin for the sorption of Cs(I) from near neutral solutions[29]. SEM showed high porosity of the materials. SEM-EDX analysis after Cs(I) sorption showed the structure to be more compact. Sorption of individual metals under comparable concentrations of Cs(I) followed the sequence: Na(I) < Rb(I) < $NH^{4+}$. The stability of the sorbent was evidently demonstrated by the low release of Ni and Fe during sorption process, and by the apparent stability of Cs(I) during KCl elution confirmed the strong interaction of cesium with the inorganic ion-exchanger.

Chitosan-tripolyphosphate (CTPP) beads prepared using in-liquid curing method were used for the adsorption of uranium from aqueous solution[30]. Experiments showed the beads with higher cross-linking to have greater adsorption capacity. The U adsorption capacity of lower cross-linked beads decreased along with increase in pH of the solution.

From the FTIR characterization data of the beads before and after uranium adsorption, it is inferred that phosphate groups play a greater role in the uranium uptake by CTPP beads than the amino groups.

The successful removal of the hazardous $^{60}$Co and Eu radionuclides from aqueous solutions was done by using Chitosan benzoyl thiourea derivative[31,152,154]. X-ray diffraction studies showed lowering of the crystallinity with increasing the extent of substitution reaction.

A summary of sorption capacities and conditions of chitin- and related-derivatives for removal of different radionuclides has been presented in Table 3. It is clear from this vast literature survey the chitin- and related-derivatives have been proved to be very useful in sorption of radionuclides from different contaminated sources. The mechanism of sorption is found to be dependent on electrostatic interactions, chelation and ion pair formation. The sorption process is influenced by several factors such as pH, temperature, sorbent dosage, ion concentration, contact time, presence of competing ions, and characteristics of the radionuclide.

## Fungal Biosorption for Radionuclide Removal

The term 'Biosorption' can be used in a number of ways like bioadsorption, bioabsorption and bioaccumulation to describe sorption by living or dead biomass, bioaccumulation, etc of a diverse array of substances such as metals, radionuclides, and organics[32]. Biosorption can be done by using bacteria, plants, fungi, algae, moss, or other organic material. This review includes articles concerned with fungal biosorption as it has been found that chitin and chitosan are a major part of fungal cell wall of fungi divisions: Ascomycota, Basiodiomycota and Zygomycota. The functional groups provided by chitin and chitosan in the cell walls of these fungi play a major role in the biosorption processes of fungi.

**Table 3:** Adsorbents, Radionuclide, Adsoprtion capacity, Kinetics model & Isotherm, and Reference.

| Adsorbent | Adsorbate | Sorption Capacity (mg/g) or $K_d$ (mL/g) | Kinetic Model & Isotherm | Reference |
|---|---|---|---|---|
| Shrimp Shells containing chitin | U(VI) | 7.484 | Psuedo Second Order; Langmuir | 5 |
| Chitosan | Tc(IV), I(I), Cs(I) | $K_d$ -54, 88, 134 | - | 8 |
| Chitogran- M; Chitogran- Cs, Nano-fibrous Chitosan | U(VI), Cs(II), U(VI) | 173.74, 264.41, 952 | - | 11 |
| Chitosan | Ni(II) | 162.6 | Langmuir | 12 |
| Magnetic chitosan beads | Sr(II) | 11.58 | Langmuir | 14 |
| Magnetic Chitosan | U(VI), Th(IV) | 666.67, 312.50 | Freundlich, Langmuir, and Dubinin–Radushkevich | 15 |
| Tetraethylenepentamine modified magnetic chitosan resin | U(VI) | 428.45 | Pseudo first order and pseudo second order; Freundlich, Langmuir, and Dubinin–Radushkevich | 16 |
| Cobalt (II) imprinted chitosan | Co(II) | - | - | 17 |
| Chitosan | I(I) | $K_d$ -88 | - | 18 |
| Poly(methacrylic acid)-grafted chitosan/bentonite (CTS-g-PMAA/Bent) composite (Prepared via Graft Copolymerization) | U(VI) | 117.2 | Psuedo Second Order; Langmuir | 19 |
| Poly(methacrylic acid)-grafted chitosan/bentonite (CTS-g-PMAA/Bent) composite | Th(IV) | 110.6 | Psuedo Second Order; Langmuir | 20 |
| Chitosan/clinoptilolite | U(VI), Th(IV) | 328.32, 408.62 | Psuedo Second Order; Langumir, Freundlich & Sips | 21 |
| Cross-linked chitosan (CRC) | UO2(II), Th(IV), Cs(I), Eu(III) | $K_d$ -125, 44.7, 24.3, 1.54 | - | 22 |
| Cross-linked chitosan after hydrolysis (CRCH) | Th(IV), Cs(I), Eu(III), U(VI) | $K_d$ -203, 149, 125, 18.0 | - | 22 |
| Chitosan grafted with citric acid | U(VI) | 22.3 | Psuedo Second Order; Langmuir, Freundlich and Redlich-Peterson | 23 |
| Natural Chitin, Dithizone-Modified Chitin | Co(II) | 27.25, 30.58 | Psuedo First Order; Freundlich | 25 |
| Chitosan modified MWCNTs (Prepared via Chemical Vapour Deposition and Low temperature plasma technique) | U(VI) | - | Langmuir | 26 |
| Carboxymethylated chitosan (CMCts) (Prepared via Gamma-ray irradiation) | Sr(II) | 99 | Langmuir | 27 |
| Chitosan cryogel modified with pyridoxal-5´-phosphate | Eu(III) | 7.85 | Langmuir | 28 |
| Nickel–potassium ferrocyanide immobilized onto chitosan foam | Cs(I) | 81 | Psuedo Second Order; Langmuir | 29 |
| Chitosan-tripolyphosphate (CTPP) | U(VI) | 239.9 | Psuedo Second Order; Langmuir and Freundlich | 30 |
| Chitosan benzoyl thiourea derivative | Co(II), Eu(III) | 29.47, 34.54 | Langmuir, Freundlich & Lagergren | 31 |
| *Rhodosporidium fluviale* strain UA2 | Cs(II) | 0.182 | Langmuir | 33 |
| *Pleurotus mutilus* | U(VI) | 250 | Psuedo Second Order; Langmuir and Freundlich | 34 |
| *Schizophyllum commune* 4–39 (CYM-T culture medium) | U(VI) | 240-280 | - | 35 |
| Immobilized cells of *Rhodotorula glutinis* | U(VI) | 17.3 | Psuedo First Order; Sips | 36 |
| Ca-alginate immobilized Trichoderma harzianum | U(VI) | - | - | 37 |
| Potassium nickel hexacyanoferrate-modified *Agaricus bisporus* | Cs(II) | 6.576 | Psuedo Second Order; Freundlich | 38 |
| *Fusarium* sp. #ZZF51 in pure form, formaldehyde, methanol, and acetic acid treated forms. | U(VI) | 21.42, 318.04, 311.95, 351.67 | Psuedo Second Order; Langmuir and Freundlich | 39 |
| Magnetically modified *Rhodotorula glutinis* | U(VI) | 73.5 | Psuedo First Order; Langmuir | 40 |

| | | | | |
|---|---|---|---|---|
| *Geotrichum* sp. Dwc-1/attapulgite (Prepared via Hydrothermal Process) | U(VI) | 125 | Psuedo Second Order, Psuedo First Order; Langmuir and Freundlich | 41 |
| *Rhodotorula glutinis* in pure form, methanol, and formaldehyde treated | U(VI) | 98.4, 129,110 | Langmuir and Freundlich | 42 |
| Immobilized *Aspergillus fumigatus* | U(VI) | 7.2 | Psuedo Second Order; Freundlich and Tempkin | 43 |
| *Rhizopus arrhizus* biomass cross-linked with formaldehyde | Am(II), U(VI) | 62, 68 | - | 44 |

Fungal biosorption is very promising for the remediation of radionuclides from diverse contaminated environmental sources, it also offers opportunity for use in recovery and preconcentration of commercially important radionuclides from natural sources in which radionuclides are present in largely diffused quantities.

### Live Biomass

The biosorption behavior and mechanism of $^{137}$Cs on *Rhodosporidium fluviale* (R. fluviale) strain UA2[33]. It was seen that the biosorption of $^{137}$Cs on the strain UA2 of R. fluviale was fast and was also a pH-dependent process. A substantial amount of $^{137}$Cs adsorption on UA2 was observed within the range of pH 3-9, and the optimum pH was found to be 5.0. The contact time was found to be 4 hours. $HNO_3$ was found to be an efficient eluent with a desorption percentage of 82.6.

### Dead Biomass

Dead fungal biomass (*Pleurotus mutilus*) was used for removal and recovery of U(VI) from aqueous solutions via biosorption[34]. FTIR analysis before and after uranium adsorption, demonstrated the role of amino, carboxylic, sulfonates and phosphates functional groups in the adsorption process. SEM shows the fungal biomass has rough porous surface and the micropores increase the total mass transfer area along with decreasing diffusion resistance. The maximum capacity of 250 mg/g was obtained at particle size of 250–315 um. Increasing stirring speed causes diffusion of uranium into boundary layer adsorption thus raising the diffusion coefficient. The biosorption process is exothermic in nature. Maximum adsorption capacity increased with increasing initial uranium concentration in solution, but the rate of uranium adsorbed decreases.

Sorption of Uranium by *Schizophyllum commune* from aqueous solution was examined[35]. At initial uranium concentration of 50 mg/l, binding capacities of 120–150 mg uranium per g dry weight were obtained and found to be independent of pH. Analysis via a combination of imaging techniques including HAADF and STEM showed the ions to be accumulated on both, the cell wall and intracellular. In *S. Commune*, the carboxylic groups were found to be in Uranium complication.

Biosorption of uranium ions from diluted solution onto immobilized *Rhodotorula glutinis* was carried out in a batch reactor[36]. Sips isotherm model was found to be the best. Kinetic data correlated with the pseudo-first-order model. The sorption process was found to be endothermic and spontaneous from the data obtained from the free energy value.

### Modified Biomass

Ca-alginate immobilized *Trichoderma harzianum* has been used for the adsorption of uranium ions from aqueous solution[37]. Immobilization of *Trichoderma harzianum* to Ca-alginate increased the stability and uranium biosorption capacity of the bio-adsorbent at 28 ± 2°C and 200 rpm. Ca-alginate immobilization clearly improved biosorption capacity of uranium and the stability of the biosorbent as indicated by the experimental results. Sorbed uranium was also recovered in 200 ml of 0.1 N HCl with greater than 99% of recovery.

Potassium nickel hexacyanoferrate(II) (KNiFC) modified *Agaricus bisporus* was studied for cesium ion adsorption[38]. The distribution coefficient was at interval 7,662–159 cm$^3$g$^{-1}$. From the desorption experiments it was found that 0.1 M potassium chloride was the most effective desorption agent but the complete desorption of Cs ions from KNiFC-modified biosorbent could not be attained.

Adsorption of U(VI) from waste water was carried out using *Fusarium sp. #*ZZF51 biomass, a mangrove endophytic fungus originated from South China Sea coast[39]. To enhance the affinity of uranium sorption, the fungus was treated with formaldehyde, methanol and acetic acid which resulted in methylation of amino groups, esterification of carboxyl groups, and acetylation of hydroxyl and amino groups, respectively. The following chemical modification lead to an increase in functional providing more sites for uranium binding. The maximum biosorption was obtained with acetic acid treated biomass. FTIR analysis data indicated the functional groups to play a key role in biosorption phenomenon.

In a batch system, the ability of magnetically modified *Rhodotorula glutinis* to adsorb Uranium from aqueous solution was examined[40]. With increasing biomass dosage from 0.5 mg to 10 mg, uranium sorption ratio increased. Sorption was found to be more efficient in dilute solutions as a sorption ratio of 90% was obtained for <50 mg/L uranium concentration. Experimental effects for different competing cations showed little effect on uranium sorption. The sorption process is endothermic and spontaneous implying it becomes favourable at higher temperature.

A novel adsorbent of fungus/attapulgite (F/ATP) composites was synthesized to study the removal of U(VI) from a simulated aqueous solution[41]. The thermodynamic data implied that the process was spontaneous and endothermic. Adsorption-desorption experiments indicated high sorption capacity of U(VI) (91%) over six cycles.

In order to study the role played by various functional groups in the cell wall, chemically modified yeast cells of *Rhodotorula glutinis* were used for the biosorption of Uranium[42]. Esterification of the carboxyl groups and methylation of the amino groups present in the cells were done by methanol and formaldehyde treatments, respectively. The biosorption process was found to be mainly dependent on ionic interaction and complexion formation. Amino and carboxyl groups were concluded to be the major functional groups that took part the in uranium sorption process.

Biosorption of uranium (VI) particles by immobilized *Aspergillus fumigatus* globules was explored in a batch experiment[43]. The change and the refinement of non-feasible *Rhizopus arrhizus* biomass were examined through immobilization[44]. The experiment was done at three different pH and most showed an absorbance of 95%.

Table 3 summarizes the sorption capacity and conditions of reaction for different fungi and modified fungal derivatives for radionuclide removal, respectively.

## CONCLUSIONS AND FUTURE PERSPECTIVES

This review paper indicates that adsorption using chitosan composites is becoming a promising alternative to replace traditional adsorbents in removing radionuclides from industrial waste water, ground water and effluents. The effectiveness of the treatment depends not only on the properties of the adsorbent and adsorbate, but also on various environmental conditions and parameters taken into account for the adsorption process like pH, ionic concentration, temperature, existence of competing ions in solution, initial radionuclide concentration, contact time, rpm and adsorbent dosage. These parameters should be taken into account while examining the potential of chitin/chitosan-derivatives. Due to its high hydrophilicity, flexibility of polymeric chain and large number of primary amino groups, chitosan can be regarded as a good adsorbent for radionuclides like U(VI). Different experimental studies have revealed the high potential for adsorption of such impurities from the aqueous medium by chitin, chitosan and their derivatives. One of the major advantages of the use of these composites is the cost factor i.e. the feasibility of the processes to be carried out in large scale operations. Chitosan composites are one of the chitosan-based materials that are economically feasible because they are easy to synthesize and include inexpensive chemicals. There have also been studies on the possibilities of integrating biological removal of toxic components from sewage and other wastes. It is clear that some biosorption methodologies for the treatment of heavy metals and radionuclide containing effluents offer potentially effective and economical alternatives to existing treatment technologies. Not only efficient adsorption, but adsorption-desorption studies have also revealed the highly efficient reusability of the chitin, chitosan and their derivatives along with the fungal biomass. This could dramatically lower down the cost of this downstream processing step before releasing the treated water or effluent into the environment safely. This field has a lot of potential of improvement and studies are still going on how to make the processes more efficient and lasting in order to salvage the environment and living beings from the toxic pollutants.

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