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Biosorption of ^{137}Cs and/or ^{60}Co from Radioactive Waste Solution Simulates Using Spent Black Tea (Camellia *sinensis*) Dregs

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Abstract

Cesium-137 and cobalt-60 are major radionuclides detected in various categories of radioactive waste streams generated due to the peaceful applications of nuclear technology in our life. Both are γ emitters. Cs-137(γ= 0.662 MEV) is extremely soluble alkaline, highly radiotoxic and long lived element with half-life of 30.5 years. Co-60($T_{1/2}$ = 5.25 years) has two gamma energy peaks at 1.17 and 1.33 MEV. The two radioisotopes reported to have immense applications in medicine, industry, agriculture, research and others. Hence, the generated liquid waste streams spiked with ^{137}Cs and /or ^{60}Co need adequate treatment before their release to the environment. During recent years biosorption has gained imperative credibility because of its good performance and low cost. The present work puts forward an effective green chemistry approach to radioactive liquid waste treatment. Spent Black Tea leaves (the dregs), (SBT), have been used as biosorbent for removal of these two radionuclides from their waste simulate solutions at bench scale laboratory experiments. This study aims at evaluating the efficiency of the non–costed SBT as biosorbent for Cs-137 and /or Co-60 from hazard radioactive waste streams. The factors assumed to affect the sorption capacity and determine the suitability SBT as biosorbent for these two radiocontaminants e.g. contact time, biomass dosage, and temperature of the surrounding…were evaluated. Based on the data obtained it is recorded that ~ 90% of the radiocobalt and more than 80% of radiocesium added were removed from the waste simulate stream by the SBT at concentration 150g/L, after one week, at pH value ~ 5.4 and at ambient temperature (25±5ºC). Therefore, the present study recommends spent black tea dregs as a cost effective and an easily available biosorbent, substituted for the conventional carbon based sorbents, for radiocontaminants removal.

Keywords

Biosorption, Radioactive Waste Solution, Cobalt-60, Cesium-137, Spent Black Tea

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1. Introduction

In Egypt, nuclear technology for electricity generation is a suggested option among other recommended renewable energy resources. Radioactive wastes are generated from this implementation, variant nuclear applications, improper waste storage practices, and inappropriate conditioning and disposal of these wastes. Radionuclides present in the various wastes categories pose chemical and/or radiological toxicity threats to lower and higher living organisms. [1]

The address of radioactive wastes management, in general, is to reduce the radiological hazardous risks, consequently, to protect and improve the environment, make it a better place for people and wild life.

Most cases of treatment processes for aqueous radioactive wastes aim at splitting the waste stream into two fractions:

1) A large portion where the level of contamination in which, sufficiently low to permit its discharge to the environment safely. And

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2) A small fraction of concentrate including the bulk of radionuclides.

The most conventional methods used for the treatment of liquid radiowastes include: chemical treatment [2], evaporation [3] and ion-exchange process [4].

Sorption processes provide attractive alternatives for these conventional techniques for concentrates treatment, especially, when the sorbent is cost effective and does not require an additional pretreatment step before its application.

In the aspect of radiological safety, cobalt (Co-60) and cesium (Cs-137) are major radioactive isotopes because of their high radiotoxicity, relatively long half-lives, high solubility and transferability. In addition to their accumulation from the various applications of that radioisotopes in our daily life, Co-60 may be released into the coolant by corrosion process in the reactor .It may be present dissolved in the coolant or as particulate materials. On the other hand Cs-137 entre the coolant in the event of fuel pin failure.

Total world production of tea in 2013 was about 5.5 million metric tons. Tea is consumed by the largest number of people in the world and considered the second most popular beverage in the world after water. Canned or bottled tea drinks as well as instant tea drinks are produced on all scales by hot water extraction of tea leaves. Since the spent black tea leaves are food waste, their accumulation may cause environment problem and there is a difficulty in disposing of the spent tea leaves after the extraction. [5, 6]

In this study collected spent black tea leaves of (Camellia *sinensis*) were used as biosorbent for both radiocobalt and radiocesium. FT-IR, X- Ray Diffraction (X-RD) and Scanning Electron Microscope (SEM) analyses were applied for characterization of the SBT. The aim was to evaluate the capability of the SBT, as biosorbent, for the removal of cobalt-60 and/or cesium-137 from aqueous radioactive waste simulate. The factors that may affect the efficiency of sorption process including: mass of the used biosorbent, the initial radioactivity content, the competition of the sorbet radionuclides and temperature were studied systematically.

2.Materials and Method

2.1. Materials

The sorbent

Spent black tea leaves were collected from Cafeteria in our center. Prior to use, spent black tea biomass was oven dried at 60°C up to constant mass and preserved in desiccator till use. As food waste there are minimal if any costs involved in their preparation.

All other chemicals used in this study were of analytical grade and used without any additional purification. Dilute HCl and NaOH solutions were prepared and used to adjust the pH values of the spike radioactive waste simulate solutions.

2.2. Experimental Approach

2.2.1. Characterization of the Spent Black Tea Leaves

The vacuum dried SBT samples were analyzed in KBr discs by FT-IR spectroscopy (Jasco FT-IR-6100E, Fourier transform infrared spectrometer, Japan) in the mid region of 400–4000 cm^{-1}.

The morphological features of the sample was examined by viewing the surfaces, after covering with a thin layer of gold, using a JEOL-JXA-840A scanning electron microscope (SEM) operated at 30 kV.

X-Ray diffraction (X-RD) patterns of SBT was collected on PAN analytica X-Ray Diffraction equipment model X'Pert PRO.

2.2.2. Biosorption Study

In this study, all the biosorption experiments were carried out on batch laboratory scale by equilibrating a predetermined mass of spent black tea leaves in glass containers each having a fixed volume (20 mL) of spiked radioactive waste solution simulates. The solutions were labeled by adding predetermined contents of a carrier free radiocesium (Cs-137, $T_{½}$ = 30.5 years) or radiocobalt (Co-60, $T_{½}$ =5.25 years) or mixture of both to 20 mL tap water. The two radionuclides were purchased from Radioisotope Center Polatom Institute of Atomic Energy, Poland as cesium and cobalt chlorides. The solutions were radiometrically analyzed using 3"x3" well type NaI crystal (efficiency 85%) based on Multi-Channel Analyzer PCA-P, USA. Crap samples of the waste simulate, for each container, before adding the biosorbent were withdrawn and analyzed radiometrically to determine the initial activity. After the addition of the SBT to the containers, samples from the treated media were collected at definite time intervals and their remained radioactivity contents were also counted.

The removal capability of biosorbent to uptake the radiocontaminant was calculated as follows:

$$\text{Biouptake},\% = \frac{a_o - a_t}{a_o} x100$$

Where

a_0 = the initial activity in solution, Bq/mL.

a_t=the activity content in the solution at equilibrium time (t), Bq/mL.

On the other hand, the capacity of biosorbent (Bq/g) for removal of radionuclides can be calculated from the relation:

$$Biosorption\ capacity = a_0 - a_t \times V/m$$

Where (V) is the solution volume (mL) and (m) is the mass of the biosorbent (g).

Factors that may affect the removal efficiency of SBT for Cs-137 and/or Co-60 from the spiked waste solution simulates such biomass concentration ,activity contents, pH value, contact time, shaking and radionuclides competition were studied systematically .

3. Results and Discussion

Recently, waste products from the food industry have also been considered as adsorbents for the extraction of non-radioactive [7] and radioactive heavy metals such as uranium and thorium [8–10]. According to Aksu and Isoglu: an economical adsorbent is defined as one which is abundant in nature, or is a by-product or a waste from industry and requires little processing [11]. Given the above considerations and requirements, the present work aims at exploring the suitability of spent tea leaves as biosorbent for the removal of ^{137}Cs and /or ^{60}Co from their aqueous waste simulate solutions.

However, there have been no report on the utilization of the spent black tea leaves as biosorbent for radioactive liquid waste treatment contaminated with radiocesium and /or radiocobalt.

3.1. Characterization of the Spent Black Tea Dregs

3.1.1. FT-IR Analysis

In order to identify the functional groups of waste tea leaves , FT-IR spectra was recorded in the frequency range from 4000 to 400 cm^{-1} and are shown in Fig [1]. The spectrum shows a number of peaks due to absorption of different functional groups present. In the FTIR spectra of native spent black tea, a strong broad band observed from 3200 to 3700 cm^{-1} for hydrogen bonded O—H group of phenols and/or carboxyl. The bands around 2923 cm^{-1} and 2855 cm^{-1} are indicative of—CH_2 & —CH_3 antisymmetric and —CH_2 symmetric stretching vibrations of alkanes, respectively. In the 1600-1400 cm^{-1} spectral region, five bands were easily identified: 1644 cm^{-1} ascribed to functional groups —C=O, — C=N & — C=C, including 0-H vibrations from surface of phenolic and flavonoids compounds. These groups stretching vibrations associated with carboxylates, lactones and other similar compounds.. Stretching of— C-C aromatic, and other similar compounds.. Stretching of— C-C aromatic, and the three stretching —C-C aromatic conjugated with—C=C appeared at 1542, 1517 and 1423 cm^{-1}. The presence stretch deformation of—C-C is seen at 1025 cm^{-1}. Two distinct transmittances at 1260 cm^{-1} and 1158 cm^{-1} may be attributed to— CO—NH and CO—OH bonds stretching deformation of carboxyl, anhydride, and alcohols. The bands at 961 cm^{-1} & 671 cm^{-1} are in the 'fingerprint zone' which corresponds to C_6H_5 in plane deformation and aromatic —CH out of plane bending vibration, in the same order.

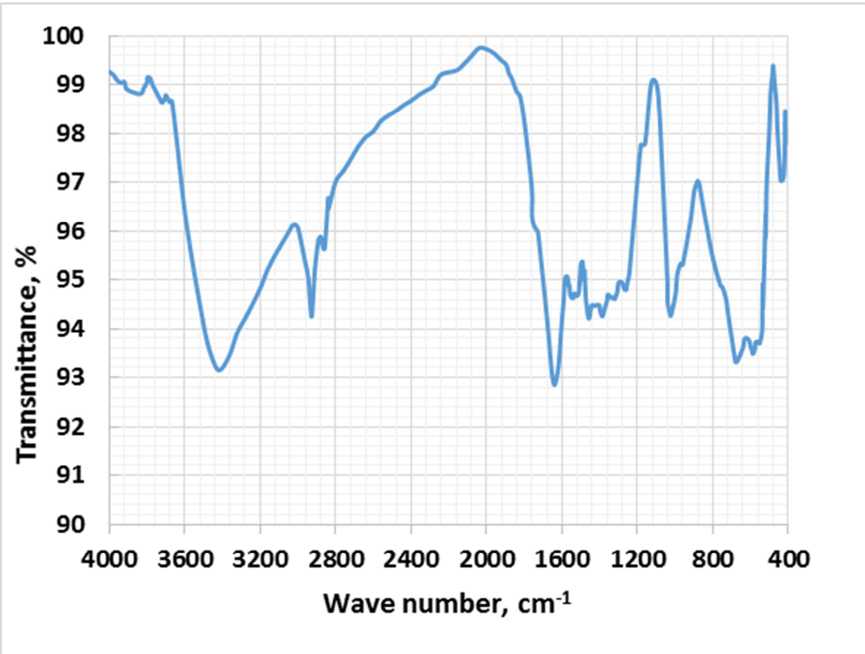


Fig. 1. Fourier transform infrared spectroscopy of the Spent Black Tea Dregs.

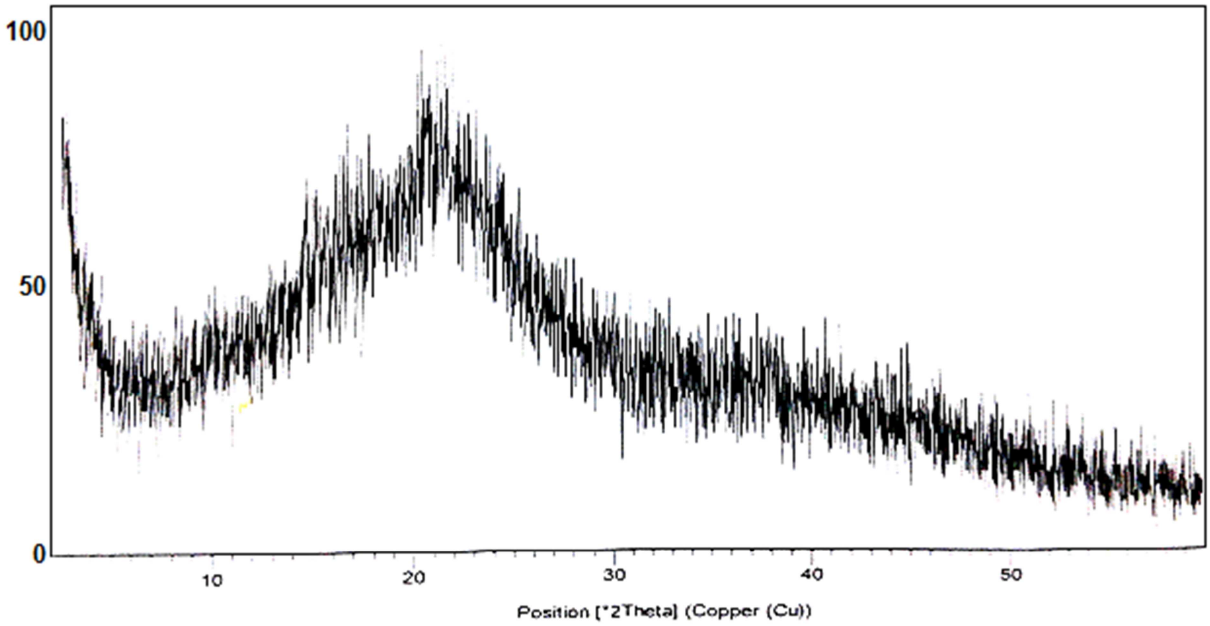


Fig. 2. X-ray diffraction pattern of Spent Black Tea Dregs.

Based on FT- IR spectroscopy, the abundant of phenolic compounds can be characterized, and the -OH groups associated with carboxylate and hydroxyl, which are predominant contributors in metal ion uptake. These significant bands in the spectrum indicated the possible involvement of functional groups on the surface of the SBT during the radioions adsorption process. [12-17].

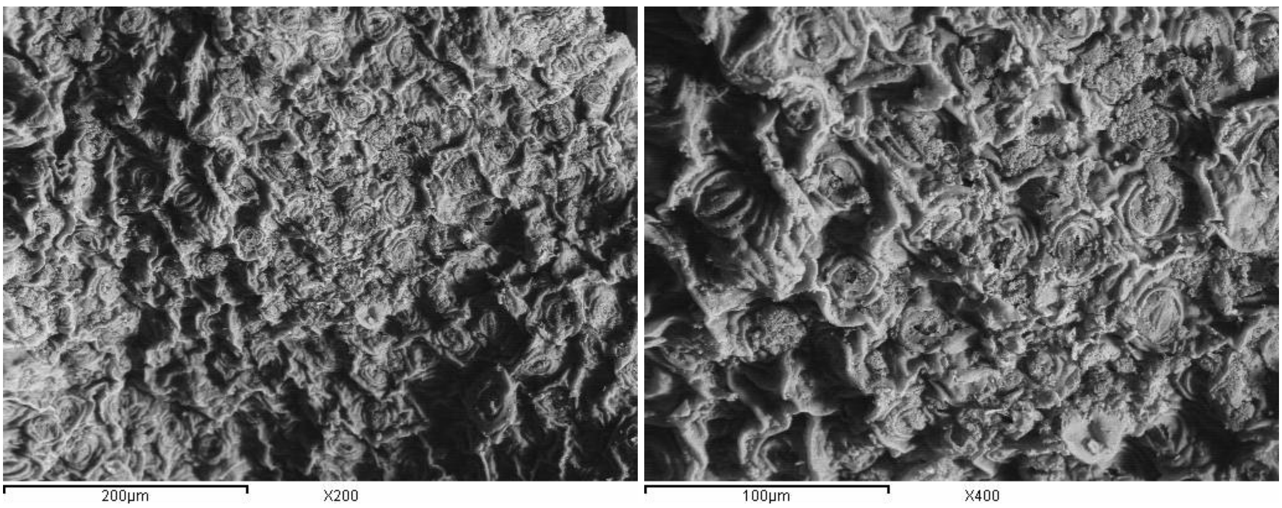
3.1.2. X-ray Diffraction Analysis

The x-ray diffractogram of the spent black tea leaves showed a hollow characteristic of an amorphous substance, fig. [2].

Due to the amorphous character of the black tea dregs' it seem to exhibit superior adsorption capability in aqueous solutions due to their high surface area and active surface functionality i.e. due to the high surface-to volume ratio of each particle, in addition to the high porosity of the sorbent.

3.1.3. Scanning Electron Microscope (SEM)

The surface morphology of the SBT was examined by scanning electron microscope. The texture of the dry leaves (sorbent) is shown in fig[3 (a-d)]. It is clear from the micrographs that particles are, to some extent, regular in shapes and exhibited more or less the same sizes, Fig. [3 (a)]. Hills and valleys can be differentiated. Fig. [3 (b)]. The surface can be seen to possess a detectable porous texture. Fig. [3(c)]. The pores are, nearly of similar sizes and shapes. There are more chances that the sorbet can be trapped in there pores or imperfections of the surface [fig.3 (d)].



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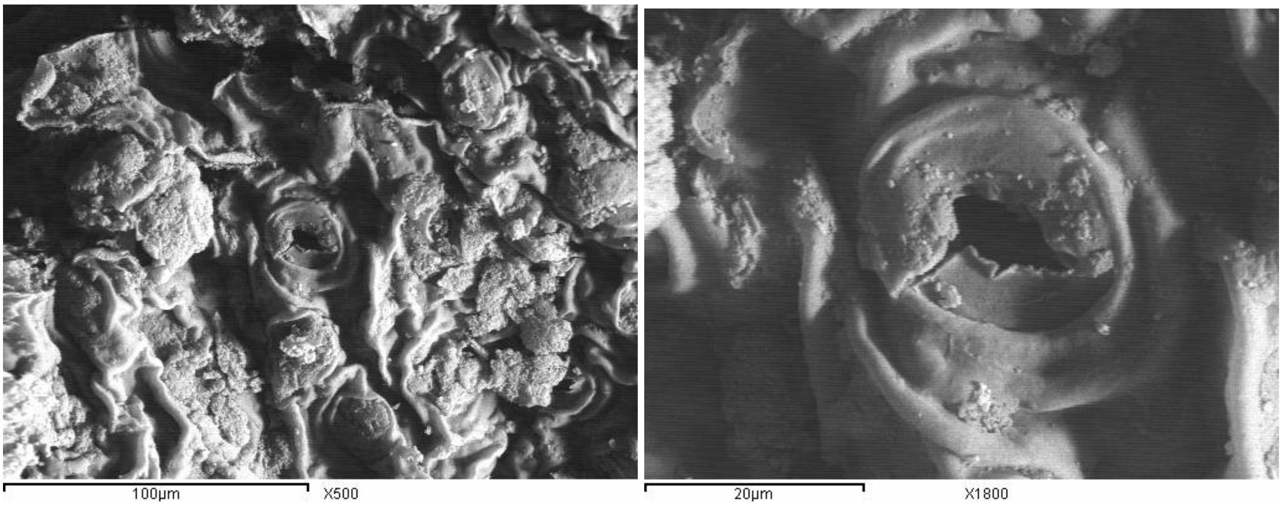

c d

Fig. 3. SEM micrographs of Spent Black Tea Dregs.

Based on the characterizations data it could be concluded that the Spent Black Tea dregs is distinguished by an amorphous surface, abundant functional sorptive groups and adequate uniformity porous surface which candidate it as cheap available biosorbent for some radiocontaminants from their liquid waste streams.

3.2. Biosorption Process

3.2.1. Effect of Contact Time

The effect of contact time on cobalt-60 biosorption at increasing sorbent concentrations (25, 50, 75,100,125 and 150g/L) was investigated and the data obtained is shown in Fig [4]. It was observed that the rate of removal of radiocobalt was rapid initially but it gradually slow down with time until it reached equilibrium. A plateau graph pattern was almost the same for all biomass concentrations. The graph showed that the maximum removal capacity of SBT reached after one week. Fig. [4] Indicated that adsorption of ^{60}Co consisted of two phases: a primary rapid phase and a secondary slower one. Up to the first day, the removal was in the rapid phase, followed by the slower sorption till one week. The biosorption capacity at room temperature (25 ± 2ºC) was more than2000 k Bq/g at equilibrium at biomass concentration 25 g/L and pH value 5.4. The primary rapid phase indicated that the rapid uptake can be due to more available sites at the beginning of the adsorption process. At the slower second phase, the active sites of the SBT dregs were occupied by radiocobalt which reduced the adsorption capacity. Comparable behavior was reported in the literatures [18].

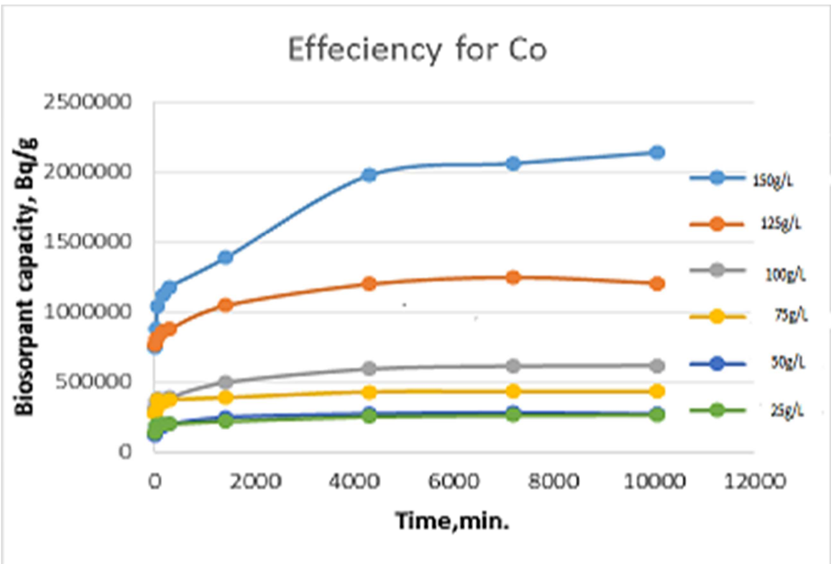

Fig. 4. The capacity of spent black tea for Co-60 as a function of increasing concentration of biosorbent.

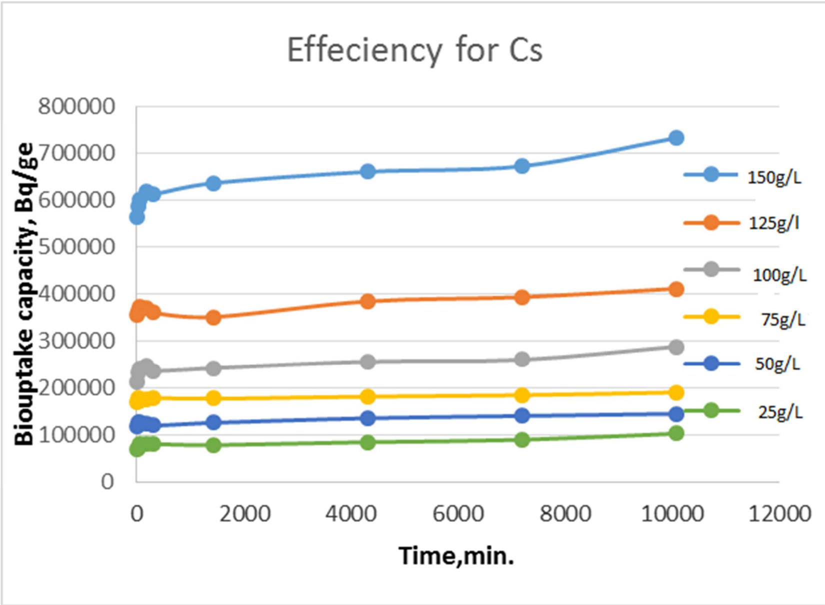

Fig. 5. The capacity of spent black tea for Cs-137 as a function of increasing concentration of biosorbent.

Under the same experimental conditions, similar trend was followed by radiocesium and the result reached is represented in Fig [5]. The biosorption capacity of the SBT to ^{137}Cs after one week is ~700 k Bq/g at equilibrium. It is worth to mention that the SBT removal capacity for both radionuclides diminished as the mass transfer driving force increased. Figs [4 & 5]. The biosorption capacity of spent tea was found to decrease as the biosorbent concentration increased from 25-150g/L. This might be due to interference between binding sites at higher concentrations or insufficiency of radiocontaminants in solution with respect to available binding sites. These results agree with that reported [19].

3.2.2. Mechanism of Biosorption

The efficiency and rate of biosorption of radionuclides into a biosorbent is function of physical and surface characteristics of the biomass, radio-ion properties and operating conditions. There are different mechanisms described the biosorption process comprises complexion, chemisorption, adsorption, ion exchange, chelation and others. The chemical structure of the biomass is of the fundamental importance in understanding the adsorption mechanism. The biosorption process persists till equilibrium is maintained between the fraction of sorbet species and its portion remaining in waste stream. The extent of the biosorbent affinity for the dissolved radiocontaminant determines its distribution between the solid and the liquid. The biosorption of radioisotopes seems to be a two steps process: the first involves interaction between the radio-ions and the reactive functional groups on the cell wall of the biomass. The radionuclides adsorption suggested that chemical interactions between the ions and the hydroxyl (OH) groups occurred on the biomass surface. The second step is an inorganic deposition of additional amounts of radioisotopes [20 & 21].

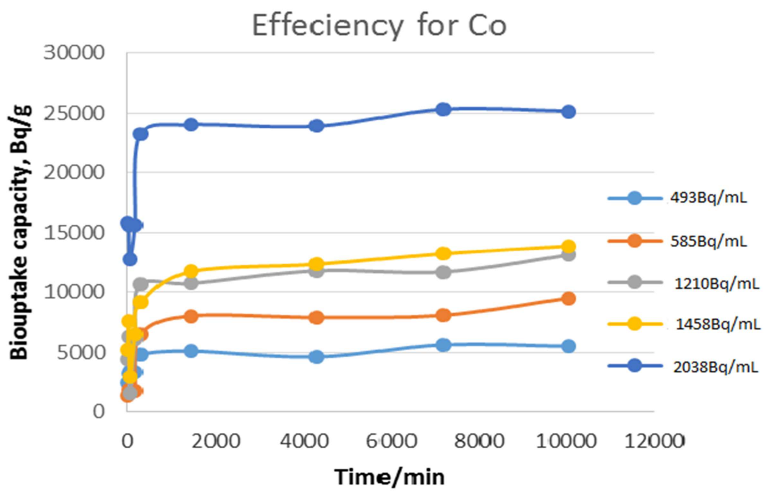

Fig. 6. The capacity of spent black tea for Co-60 as a function of initial radioactivity content.

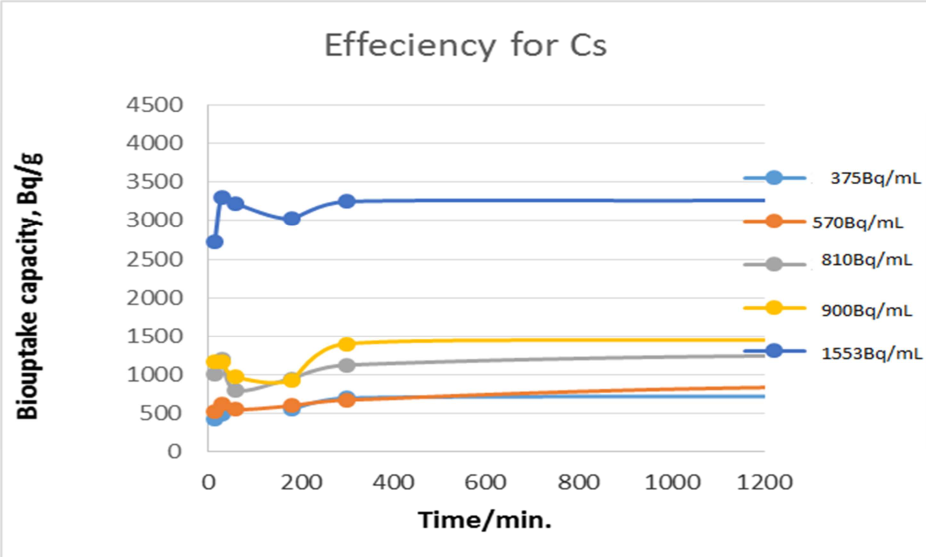

Fig. 7. The capacity of spent black tea for Cs-137 as a function of initial radioactivity content.

3.2.3. Effect of Initial Concentration

The relationship of contact time and adsorption capacity of SBT for cobalt-60 and cesium-137 onto at different initial radiocontaminants contents are shown in figures [6 & 7]. The experimental results revealed that for the all concentrations used, an initial rapid initial sorption rates followed by a slower modes were computed. The sorption efficiency was very fast from 0 time to one day, and then a nearly constant rates up to one week. An increase in capacity from more than 5 k Bq/g to more than 25k Bq/g for 60 Co and from less than 0.5 k Bq/g to about 3 k Bq/g for ^{137}Cs by raising the radiocobalt initial total activity content from 9860 to 40760Bq mL^{-1} and for radiocesium initial total activity content from 7500 to 31060 Bq mL^{-1}, respectively. The fast adsorption at the initial stage was probably due to open sorption sites allowing easy interaction with the radioions. These experimental results were explained based on the fact that, higher radioions contents enhanced the mass transfer driving force, and increased the radiocontaminants biosorbent capacity at equilibrium. Besides, with more radioions existed in solution, more active sites of the SBT were involved in the sorption process. [22]. In addition, by increasing of the radionuclides contents, the number of collisions between these radionuclides and sorbent increased, which enhanced the sorption process [23].

3.2.4. Effect of Temperature

The effect of temperature was studied by carrying out experiments at three different temperatures, 8±1, 25±2 and 60 ±1ºC. Results revealed that the sorption slightly decreased with increasing temperature, which shows that the removal of radiocontaminant by SBT is favorable at moderate temperature. Table [1]. The process seems to be an exothermic, thus the sorption is leading to a decrease in the residual forces on the surface of the SBT sorbent and may causing a decrease in its surface energy. The fact is that, progressive increase in temperature, accompanied with slightly increases in desorption of sorbet radioions and thus deactivate binding sites resulting in small decline of removal efficiency. [14].

Table [1]. The Biouptake Percentage of total activity* at increasing contact time as function of biosorption temperature.

Contact time. Hours	Temperature, ºC		
	8±1	**25±2**	**60±1**
	Biouptake*,%		
0.25	10.1	35.3	30.4
0.5	29.3	37.1	54.0
1	48.9	50.5	64.5
3	56.5	59.4	70.0
5	73.6	72.5	76.1
24	79.1	83.9	78.7
72	82.6	86.1	81.2
120	84.2	87.2	81.8
168	84.2	87.9	81.5

*The sum of Co- 60 and Cs-137 activity.

3.2.5. Effect of Shaking

The effect of shaking on the biouptake percent was studied by comparing two identical sets of experiments, one was shaken for 5 hours while the other was kept at static state for the same time .It is clear from Fig [8] that the shaking accompanied with higher biouptake percentage. This may be explain on the basis that shaking increases the mobility of radiocontaminant towards the available sorption sites and improved diffusivity of radionuclides towards well exposed sorption sites.

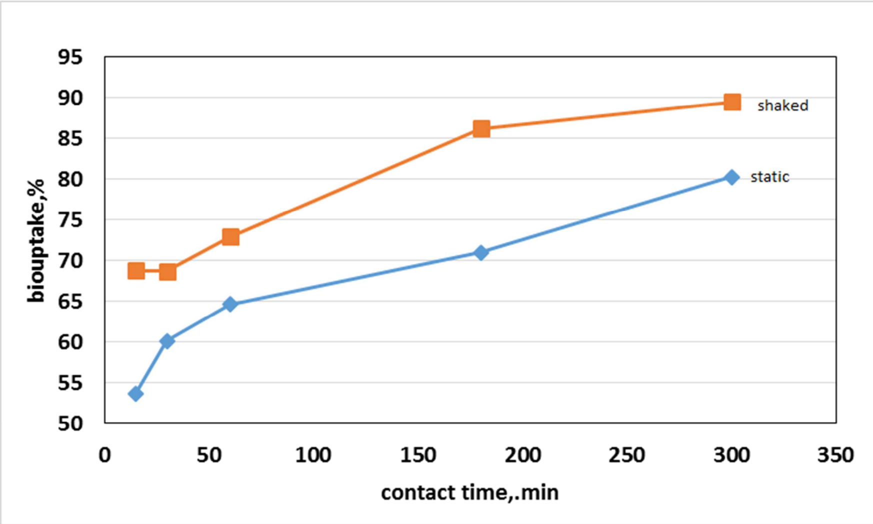

Fig. 8. The biouptake percentage of the total activity (Cs-137+ Co-60) as a function of shaking.

3.2.6. Effect of Radionuclides Competition

Both ^{137}Cs and ^{60}Co are the most predominant radionuclides found in large number of radioactive waste categories .The effect of presences of these two radionuclide on the biosorption process from waste streams spikes with both radioisotopes in single or binary composition was followed. Bench batch experiments were carried out for three aqueous waste stream simulates spiked with Cs-137, Co-60 or the both radionuclides at pH~ 5.4 and at ambient temperature equilibrated for one week. The biouptake percentage for each experiment was calculated and the results reached were represented in Fig [9]. ^{60}Co presented an adverse effect compared with the sorption of ^{137}Cs under the stated experimental conditions. The Spent Black Tea Dregs showed higher selective biosorption affinity for the Co-60 over the Cs-137. This can be attributed to the difference in the ionic radii of cobalt (192 pc) compared to the larger ionic radii of cesium one (265 pc) which facilitate its sorption on the available active sites. In addition cesium is completely soluble cation and it is assumed that sorption and desorption processes could take place simultaneously.

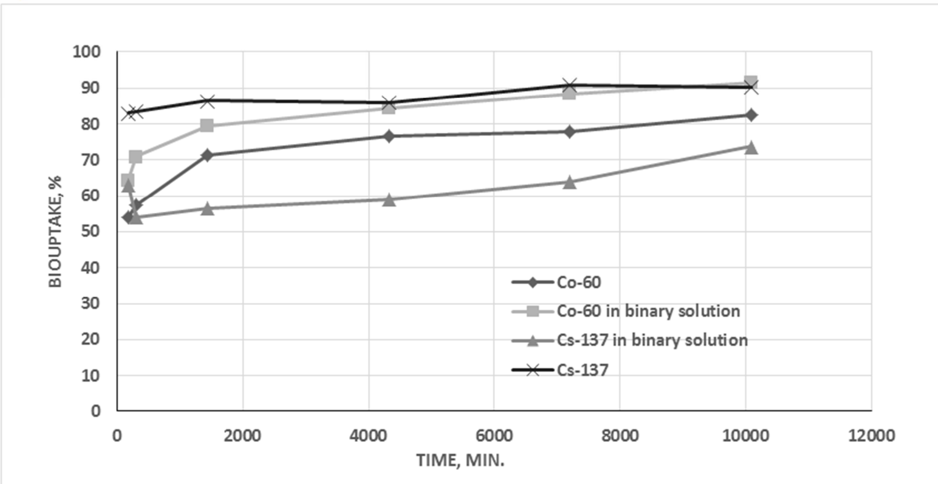

Fig. 9. The competition effect of different radionuclides on the biouptake percentage as a function of time.

3.2.7. Kinetic Approach

In order to investigate the mechanism of biosorption of radiocontaminants on the SBT, the kinetic data were analyzed based on the intra- particle diffusion equation proposed by Weber and Morris 1963.

$$R=K_{id}\,(t)^{a} \qquad (1)$$

A linearized form of this equation can be given by

$$\text{Log } R=\log K_{id} + a \log t \qquad (2)$$

Where

R = The percent of radionuclides sorbet

t = The contact time, min.

a = The gradient of linear plots

Ki_d = The intra-particles diffusion rate constant, min^{-1}

The conformity between experimental data and the modal predicated values was expressed by coefficient of determination (R^2). A relatively high value –close or equal to 1-indicates that the modal successfully can describe the kinetic of sorption process.

Fig [10] represent a plot for equation (2) linearized form for biosorption of radiocesium and radiocobalt by SBT at pH~5.4 and at ambient temperature(25±2ºC).The R^2 value is close to unity (0.9063) indicating the applicability of the intra- particle diffusion modal for this sorption process and may interpret for the two steps previously stated: The first represent the external surface sorption or instantaneous sorption state while the second is the gradual sorption stage where intra-particle diffusion seemed to be the rate controlling. Similar conclusion was reported. [24].

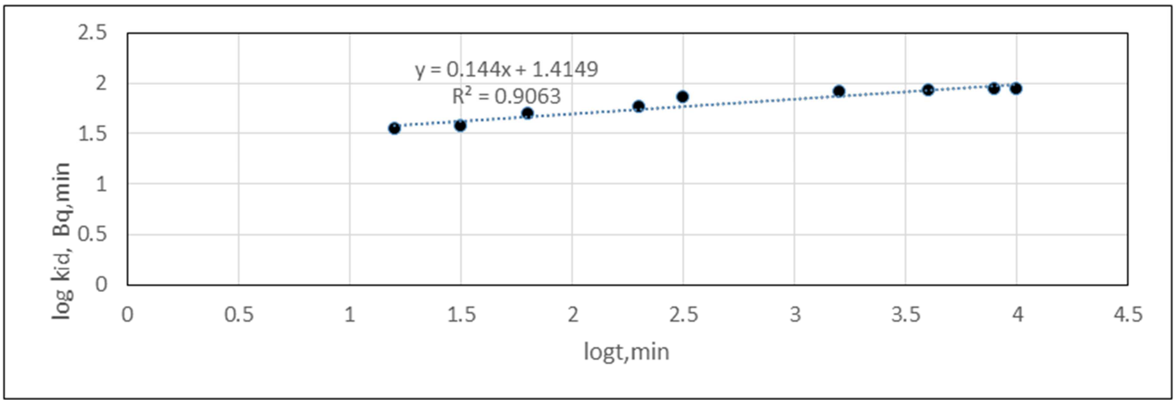

Fig. 10. Intra-particle diffusion plot for the removal Cs-137 and Co-60 by spent black tea leaves.

4. Conclusion

The present research offers an effective green chemistry approach to waste management. Biosorption process based on Spent Black Tea Leaves(dregs) provides an attractive alternatives for most conventional techniques for treatment of low and intermediate radioactive waste solution spiked with ^{60}Co and/or ^{137}Cs, especially, when the sorbent is cost effective and does not required an additional pretreatment step before its application.

The results of present investigation showed that the low cost biosorbent have comparable adsorption capacity with regard to the removal both radiocesium and/or radiocobalt from their aqueous solution. The adsorption is highly dependent on contact time, adsorbent dose, initial radioactivity content, temperature and pH. The mechanism of the sorption process seems to be based on some principal functional groups in the SBT taking part in included phenols, carboxyl and carbonyl.

The proposed spent black tea biosorbent is found to be promising candidate for the removal of radiocontaminants from waste streams, representing an economical, spontaneous, effective and environmentally perseverative utilizing waste matter.

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