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Removal of cesium from radioactive wastewater using magnetic chitosan beads cross-linked with glutaraldehyde

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Abstract A novel magnetic chitosan bead cross-linked with glutaraldehyde was prepared, characterized and applied for Cs(I) removal from aqueous solution. Characteristics and mechanism of Cs(I) removal were investigated. The equilibrium data of Cs(I) adsorption by magnetic chitosan beads were fitted using the Langmuir, Freundlich, Tempkin, Redlich–Peterson (R–P), Slips and Dubini–Radushkevich (D–R) models. The maximum adsorption capacity was estimated at 3.86 mg/g from the Langmuir isotherm. FTIR study revealed that N atom was mainly involved in Cs(I) sorption by magnetic chitosan. The magnetic chitosan is a promising adsorbing material for treating Cs(I)-containing radioactive wastewater.

Keywords Cesium · Adsorption · Magnetic chitosan · Biosorbent · Equilibrium · Mechanism

1 Introduction

After Fukushima accident in Japan, the treatment of low-level liquid radioactive waste has received unprecedented attention all over the world [1]. Radioactive wastewater is an inevitable residue from the use of radioactive materials in industry and medicine sectors, or research and nuclear establishments. The presence of radionuclides and their fission products even at low concentrations can pose serious chemical and radiological toxicity threats to living organisms [2]. Most of the combined radioactivity in liquid nuclear waste is from the fission products ^{137}Cs and ^{90}Sr. ^{137}Cs, having a half-life of 30.17 years and being easily assimilable, as an alkaline element, by living organisms, presents a serious radiological hazard [3].

The main techniques for treatment of liquid radioactive wastes include precipitation, membrane separation, ion exchange and adsorption [4]. Adsorption is regarded as a promising technique for ^{137}Cs removal. Using low-cost biosorbents may be an alternative technology for removing radioactive waste from aqueous solutions [5–8].

Recently, many researchers have reported preparation and application of magnetic chitosan for removing metal ions [9–17]. As a novel biosorbent, magnetic chitosan is advantageous to removal of heavy metals and radionuclides from aqueous solution, in its strong metal chelating capability due to the presence of amine and hydroxyl groups in chitosan chain [9], and in its easy separation from aqueous solution by using magnetic field. However, to our knowledge, there are a few reports on treatment of radioactive wastewater using magnetic chitosan.

For equilibrium adsorption description and experimental data analysis, the isotherm models of Langmuir, Freundlich, BET, Redlich–Peterson, Temkin, Toth and Slip can be used [18–21]. Suitable isotherms shall be chosen to interpret the adsorption mechanism and predict the adsorption process for magnetic chitosan.

The objective of this study was to investigate the characteristics and mechanisms of Cs(I) removal from aqueous solution by a novel magnetic chitosan beads cross-linked

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with glutaraldehyde. A simple synthesis method was used to prepare cross-linked magnetic chitosan, which was characterized before and after cesium adsorption by X-ray diffraction (XRD), energy disperse X-ray spectrometer (EDS) and Fourier transform infrared (FTIR) spectroscopy. The equilibrium sorption data were fitted using different isotherm models.

2 Materials and methods

2.1 Chemicals and materials

Chitosan flakes (85 % deacetylated) were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All other reagents used in this work were of analytical grade. CsCl was used as source for Cs(I) ions. Stock solution (1000 mg/L) of the studied ions was prepared in distilled water.

2.2 Preparation of magnetic chitosan

Chitosan flakes were added into 100 mL 3 % (v/v) acetic acid in a beaker to obtain chitosan solution and the mixture placed overnight. Fe(III) (as $FeCl_3$) and Fe(II) (as $FeSO_4$) (0.02 mol: 0.01 mol) were dissolved and added into the above mixed solution, mechanically stirred for 3 h. The beads were collected and washed with DI water until reaching neutrality. Then the magnetic chitosan beads were cross-linked with glutaraldehyde [22]. The wet beads were suspended in 0.05 M glutaraldehyde solution to obtain a ratio of 1:1 with chitosan. The chitosan beads in resulting glutaraldehyde solution were left standing for 24 h at room temperature. After 24 h, the cross-linked magnetic chitosan beads were intensively washed with distilled water, filtered and vacuum-dried at 70 °C. The newly formed beads were ground to a constant particle size (<84 μm) before use.

2.3 Characterization of magnetic chitosan

XRD patterns of the magnetic chitosan were obtained at room temperature with D/max-TTR III, Japan, using CuKα ray at $2\theta = 10°–90°$. Before and after Cs(I) adsorption of the magnetic chitosan, samples were prepared in KBr disks and FTIR spectra were recorded using an FTIR spectrometer (Spectrum GX, Perkin-Elmer), in a scanning range of 400–4000 cm^{-1}. EDS spectra of the magnetic chitosan were measured on a scanning electron microscope.

2.4 Cs(I) uptake experiments using batch method

Experiments were carried out by mixing sorbent with 15 mL of an aqueous solution of Cs(I). The mixture was agitated at 150 rpm in a temperature-controlled shaker to reach equilibrium. The solution pH was adjusted to 5.0 with 0.1 N HCl or 0.1 N NaOH aqueous solution without any further adjustment during the sorption process. Adsorption isotherms were studied at various initial concentrations of Cs(I) ion in the range of 5–50 mg/L with the sorbent dosage of 20 mg/15 mL. After adsorption, the samples was separated from the sorption system by using magnetic field and analyzed for their Cs(I) content by atom adsorption spectrum (AAS6, VARIO).All experiments were conducted in triplicate.

The equilibrium adsorption capacity was calculated from the mass balance equation as

$$q_e = (C_0 - C_e)V/W, \tag{1}$$

where q_e is the equilibrium adsorption capacity (mg/g); C_0 and C_e are initial and equilibrium concentrations (mg/L) of Cs(I), respectively; V is volume of the Cs(I) solution (L); and W is the weight of magnetic chitosan (g).

2.5 Adsorption isotherms

The following six adsorption isotherms were used to model the cesium adsorption by magnetic chitosan beads:

The Langmuir model (see Sect. 3.2 for detailed explanations of the models):

$$q_e = q_m k_L C_e/(1 + k_L C_e) \tag{2}$$

The Freundlich model:

$$q_e = k_F C_e^{1/n} \tag{3}$$

The Temkin model:

$$q_e = (RT/b) \cdot (\ln A + \ln C_e) \tag{4}$$

The Redlich–Peterson model [20]:

$$q_e = k_{RP} C_e \big/ \left(1 + \alpha_{RP} C_e^{\beta}\right) \tag{5}$$

The Slips (or Langmuir–Freundlich) model [21]:

$$q_e = k_S C_e^{1/b} \Big/ \left(1 + \alpha_S C_e^{1/b}\right) \tag{6}$$

The Dubinin–Radushkevich (D–R) model [22]:

$$q_e = q_{m} \cdot \exp\left(-k_{DR} \varepsilon^2\right) \tag{7}$$

3 Results and discussion

3.1 Characterization of magnetic chitosan

XRD analysis was used for the fingerprint characterization of crystalline materials. As shown in Fig. 1, XRD

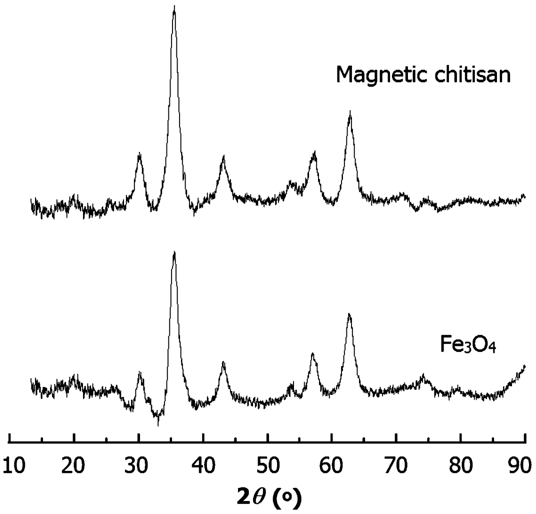

Fig. 1 XRD patterns of magnetic chitosan and Fe_3O_4

patterns of the magnetic chitosan and pure Fe_3O_4 have similar peaks. Six characteristic peaks for Fe_3O_4 ($2\theta = 30.1°$, $35.5°$, $43.3°$, $53.4°$, $57.2°$ and $62.5°$) were observed in both the spectra. This indicates the existence of ferroferric oxide particles (Fe_3O_4) in magnetic chitosan, which can be used for the magnetic separation.

Figure 2 shows an SEM image of magnetic chitosan bead and the EDS spectrum that confirms the existence of chitosan and Fe_3O_4, by the peaks of C, O, N and Fe, which are major constituents of chitosan and magnetite.

3.2 Adsorption isotherms

Figure 3 shows the Cs(I) adsorption equilibrium isotherm of magnetic chitosan. The adsorption capacity increases with the equilibrium concentration of Cs(I) in solution, progressively saturating the adsorbent.

Equilibrium isotherm models can be used to describe the experimental adsorption data and provide insight into the sorption mechanism, the surface properties and the affinity between sorbent and sorbate [19]. The Langmuir isotherm model is representative of monolayer sorption occurring on energetically uniform surface on which the adsorbed molecules are not interactive. Accordingly, equilibrium is attained once the monolayer is completely saturated. The Freundlich model describes the sorption on an energetically heterogeneous surface on which the adsorbed molecules are interactive and the amount of solute adsorbed increases infinitely with the concentration. The Tempkin isotherm is a model related to the heat of adsorption. The Redlich–Peterson equation contains three parameters and incorporates features of the Langmuir and Freundlich isotherms. Dubinin–Radushkevich isotherm model was applied to determine the sorption type (physical or chemical sorption), which is more general than the Langmuir model because it does not require homogenous sorption sites or constant sorption potential.

For the Langmuir isotherm, q_e is the amount of adsorption (mg/g) and C_e is the sorbate concentration on solution (mg/L), both at equilibrium; k_L is the Langmuir constant (L/mg) related to the energy of sorption; and q_m is the maximum sorption capacity (mg/g) for monolayer formation on sorbent. For the Freundlich isotherm, k_F is the Freundlich constant for the adsorption capacity (mg/g) and n is the adsorption intensity. In the R–P equation, k_{RP}, α_{RP} and β are R–P parameters; β lies between 0 and 1, and at $\beta = 1$, the R–P equation becomes the Langmuir form; when k_{RP} and α_{RP} are much greater than unity, the equation can transform to the Freundlich form. For the D–R model, k_{DR} gives the mean free energy E (kJ/mol) of sorption, which can be calculated as:

$$E = 1/(2k_{DR})^{1/2}. \tag{8}$$

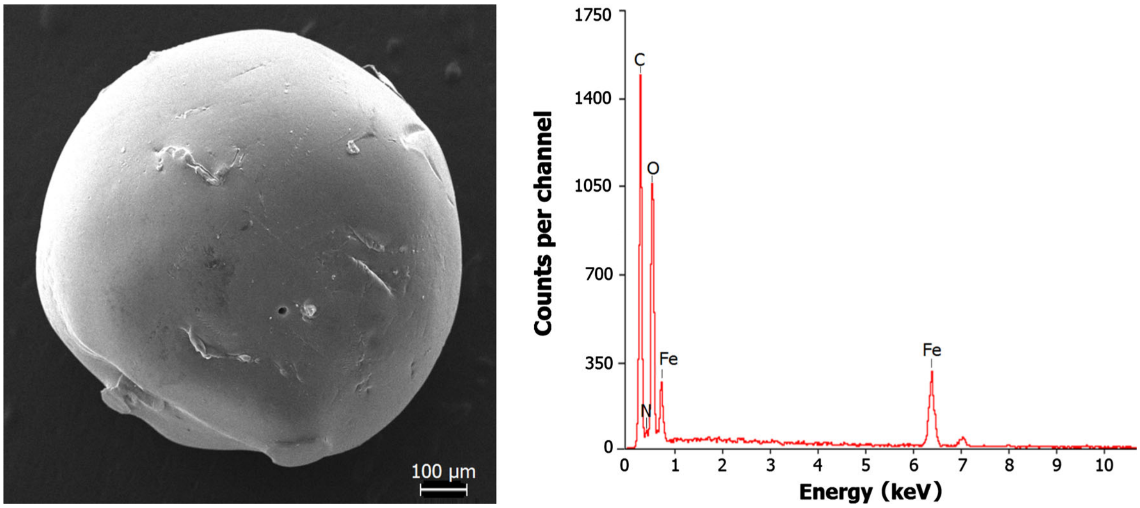

Fig. 2 SEM image and EDS spectrum of the magnetic chitosan bead

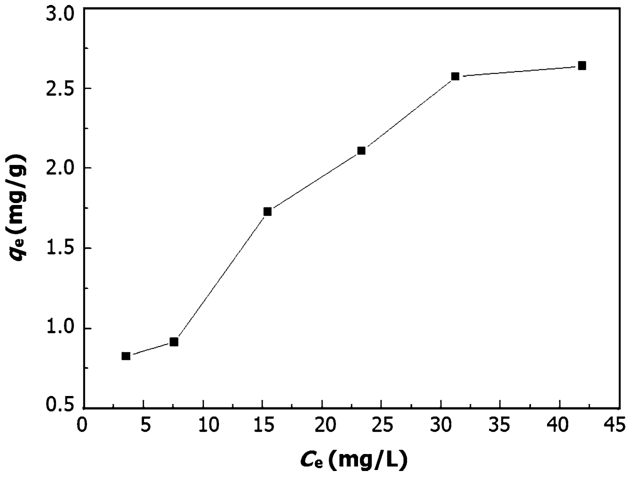

Fig. 3 Equilibrium Cs(I) adsorption isotherm of magnetic chitosan

For $E = 8$–16 kJ/mol, the process is chemical sorption, while for $E < 8$ kJ/mol, the process is of a physical nature.

The experimental data in this work were compared by using the six isotherm models, for the best-fitted models and parameters. Parameters of the Langmuir, Freundlich, Tempkin and the D–R models were obtained by linear regression analysis. For R–P and Slips isotherms, the model parameters were estimated by nonlinear regression.

The plots of Cs(I) adsorption of by magnetic chitosan using six adsorption isotherm models are shown in Fig. 4, and the calculated constants are given in Table 1. It can be seen that the Freundlich model is the best of all the models in describing the sorption data, indicating that magnetic chitosan is heterogeneous in surface properties. In the Freundlich model, the *n* value is 1.87 (in the range of 1–10), indicating that the sorption process was favorable. The maximum sorption capacity calculated from the Langmuir isotherm was 3.86 mg/g. However, the maximum sorption capacity derived from the D–R model was quite different. This may attributed to the different assumptions considered in the formulation of the isotherms. The differences were also reported by Krishna et al. [19]. The value of $E = 11.2$ kJ/mol indicates that the removal process is chemical sorption.

Li and Bai [23] studied copper adsorption on chitosan–cellulose hydrogel beads. The adsorption isotherm data were analyzed by the Langmuir and Freundlich models, and the results showed that Cu(II) adsorption by the cross-linked chitosan–cellulose could be well described by just the Freundlich model, suggesting that the cross-linked chitosan–cellulose beads were heterogeneous.

Dinu and Dragan [24] reported that Cu(II), Co(II) and Ni(II) ion removal from aqueous solution using a novel chitosan/clinoptilolite composite and the analysis of equilibrium data were tested by the Freundlich and Langmuir isotherm models. Based on their calculated constants, the experimental data obtained for adsorption of the metal ions onto chitosan/clinoptilolite composite well fitted in the Langmuir model. Similar trend was observed by Ngah et al. [25] for the adsorption of Fe(II) and Fe(III) on chitosan and cross-linked chitosan beads.

The equilibrium adsorption of Cd(II) from wastewater on cross-linked chitosan/polyvinyl alcohol blend beads obeyed both Langmuir and Freundlich isotherms [26].

About adsorption capacity, Ebner et al. [27] reported that the maximum adsorption capacity of Cs(II) on magnetite was 0.187 mg/g at pH 6.0.

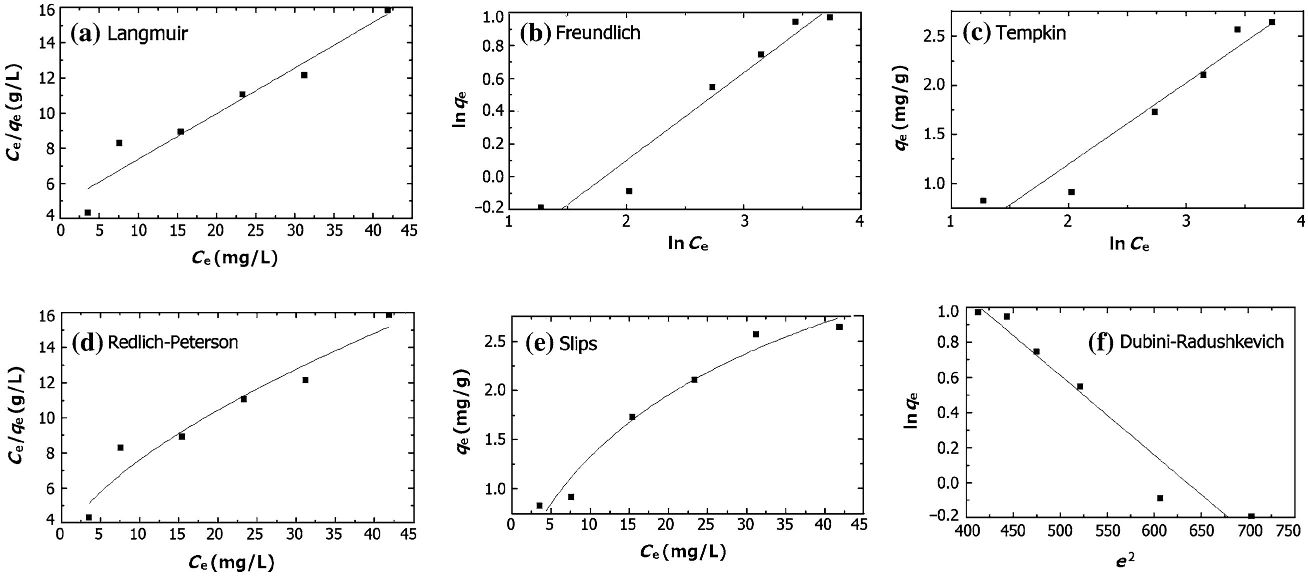

Fig. 4 Plots for Cs(I) adsorption by magnetic chitosan using six adsorption isotherm models

Table 1 Equilibrium parameters for Cs(I) adsorption by magnetic chitosan

Model	Constants
Langmuir	$k_L = 0.0542$ L/mg, $q_m = 3.86$ mg/g, $R^2 = 0.934$
Freundlich	$k_F = 0.378$ mg/g, $n = 1.87$, $R^2 = 0.951$
Tempkin	$A = 0.577$, $B = 0.826$, $R^2 = 0.940$
Redlich–Peterson (R–P)	$k_{RP} = 0.409$ g^{-1}, $\alpha_{RP} = 0.494$ g$^{-\beta}$, $\beta = 0.631$, $R^2 = 0.905$
Sips	$k_S = 0.279$ L^b mg^{1-b} g^{-1}, $\alpha_S = 0.0508$ (L/mg)^b, $b = 1.26$, $R^2 = 0.948$
Dubini–Radushkevich (D–R)	$q_m = 17.7$ mg/g, $K = 4 \times 10^{-3}$ mol^2 k^{-1} J^{-2}, $E = 11.2$ kJ/mol, $R^2 = 0.945$

So, the sorbent developed in the present study exhibits higher adsorption capacity compared to other sorbents.

3.3 Adsorption mechanism of Cs(I) on magnetic chitosan

To determine the main functional groups which are responsible for Cs(I) binding and elucidate the adsorption mechanism, the surface interactions involved in the adsorption process (with pH 5.0) were examined. FTIR spectra of magnetic chitosan were collected before and after Cs(I) adsorption. As shown in Fig. 5, the peaks at 3357 and 2866 cm^{-1} are attributed to O–H and C–H stretching vibration, respectively. The absorption bands at 1153 cm^{-1} (asymmetric stretching of the C–O–C bridge), 1261 cm^{-1} (C–N stretching), 1067 and 1030 cm^{-1}(skeletal vibrations involving C–O stretching) are characteristics of saccharide structure of chitosan [28–30]. The peak at 579 cm^{-1} corresponds to Fe–O group proving the existence of Fe_3O_4. The band at 1594 cm^{-1} for magnetic chitosan can be assigned to the –NH group in amine. Because the magnetic chitosan was cross-linked by glutaraldehyde, a peak at 1648 cm^{-1} was observed, which corresponds to the stretching vibration of C=N bond. This peak indicates the formation of Schiff's base as a result of the reaction between carbonyl group of glutaraldehyde and amine group of chitosan chains [31]. After adsorption, the peak at 1648 cm^{-1} (assigned to the C=N group) shifted to 1641 cm^{-1} and reduced intensity of peak at 1594 cm^{-1} (assigned to the –NH group in amine) can be observed, indicating the participation of N atom in the reaction between sorbent and Cs(I). It can be seen from the FTIR spectra that N atom was mainly involved in the adsorption process.

Similar behaviors were observed by other researchers [23, 32], who concluded that Cu adsorption on the beads mainly involved in the nitrogen atoms in chitosan to form surface complexed through FTIR spectroscopy.

FTIR spectra analysis of magnetic chitosan before and after Cs(I) adsorption suggests the participation of N atom in the reaction between magnetic chitosan and Cs(I); i.e., N atom was mainly involved in the adsorption process, and the possible reactions may be as follows:

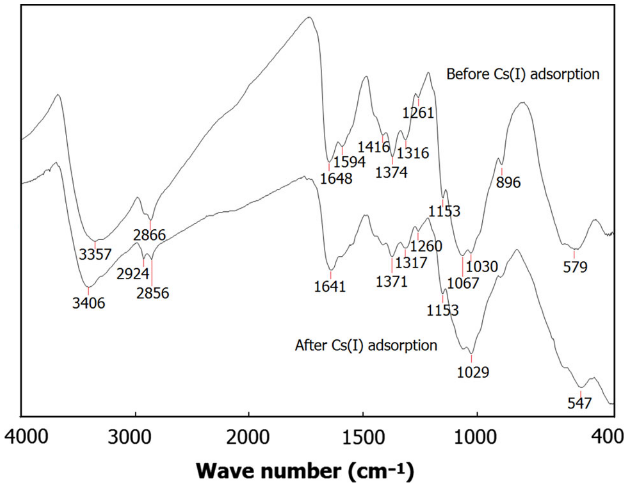

Fig. 5 FTIR spectra of magnetic chitosan before and after adsorption of Cs(I)

$$\mathrm{R{-}NH_2 + Cs^+ \rightarrow R{-}NH_2Cs^+} \tag{9}$$

$$\mathrm{R{-}NH_2 + H^+ \rightarrow R{-}NH_3^+} \tag{10}$$

$$\mathrm{R{-}NH_3^+ + Cs^+ \rightarrow R{-}NH_2Cs^+ + H^+} \tag{11}$$

Because the electrostatic attraction between N atoms and Cs^+ is stronger than that between N atoms and H^+, the magnetic chitosan is favorable for adsorption cesium ions rather than hydrogen ions.

4 Conclusion

A novel magnetic chitosan was obtained, characterized and used for removing Cs(I) from aqueous solution. The equilibrium data were fitted using six different isotherm models, and the results showed that the Freundlich isotherm was most suitable. The maximum adsorption capacity of magnetic chitosan for Cs(I) was calculated to be 3.86 mg/g. FTIR analysis showed that N atom participated in the Cs(I) removal process by magnetic chitosan.

The magnetic chitosan is promising for treating the Cs(I)-containing wastewater.

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