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Selective cesium removal from radioactive liquid waste by crown ether immobilized new class conjugate adsorbent

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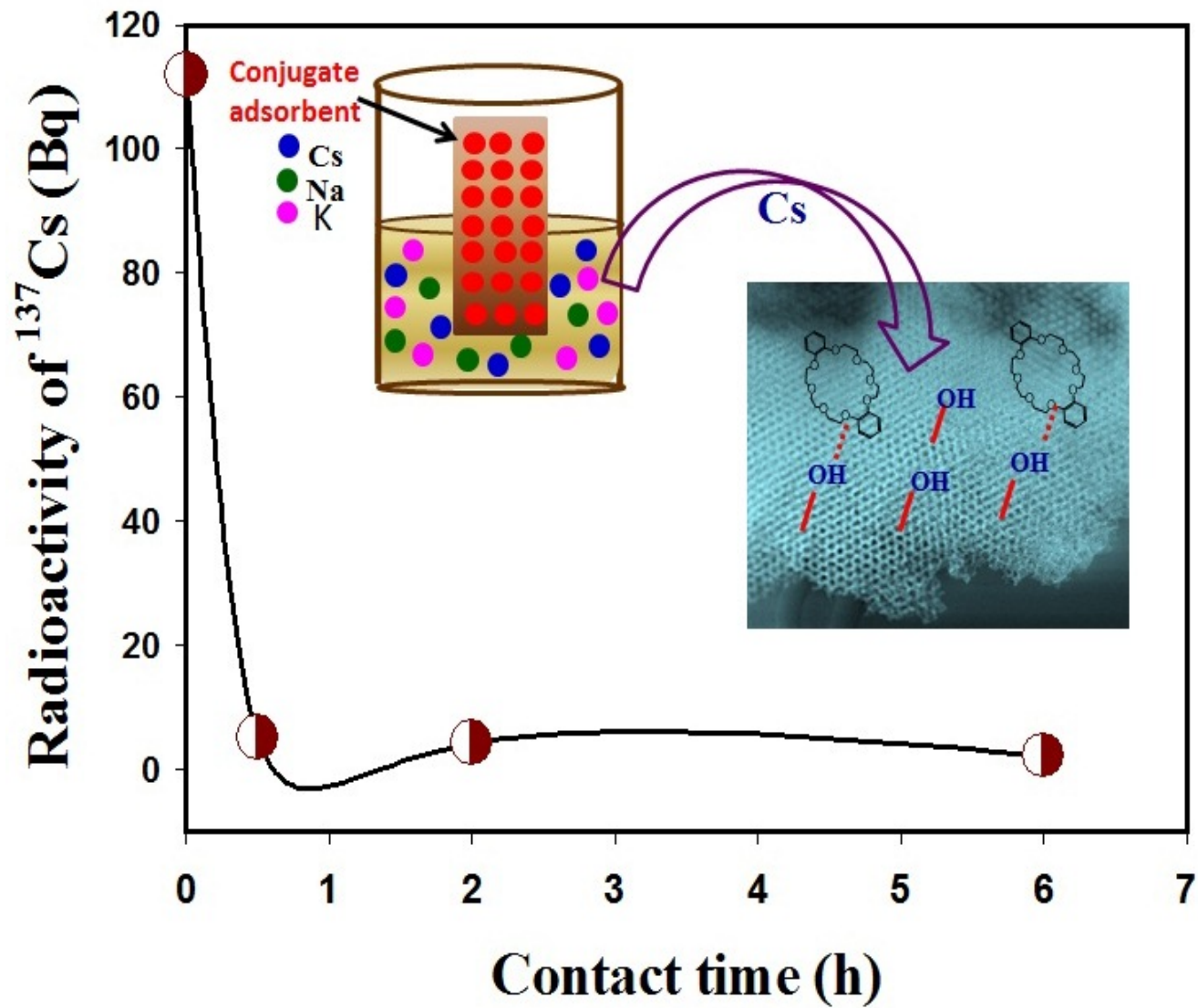
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Research highlights:

- DB24C8 crown ether was functionalized for preparation of conjugate adsorbent.
- Radioactive ¹³⁷Cs can be selectively removed by the conjugate adsorbent.
- Adsorbent can effectively capture Cs even in the presence of a high amount Na & K.
- Adsorbent is reversible and able to be reused without significant deterioration.

Graphical Abstract



ABSTRACT

Conjugate materials can provide chemical functionality, enabling an assembly of the ligand complexation ability to metal ions that are important for applications, such as separation and removal devices. In this study, we developed ligand immobilized conjugate adsorbent for selective cesium (Cs) removal from wastewater. The adsorbent was synthesized by direct immobilization of dibenzo-24-crown-8 ether onto inorganic mesoporous silica. The effective parameters such as solution pH, contact time, initial Cs concentration and ionic strength of Na and K ion concentrations were evaluated and optimized systematically. This adsorbent was exhibited the high surface area-to-volume ratios and uniformly shaped pores in case cavities, and its active sites kept open functionality to taking up Cs. The obtained results revealed that adsorbent had higher selectivity towards Cs even in the presence of a high concentration of Na and K and this is probably due to the Cs- π interaction of the benzene ring. The proposed adsorbent was successfully applied for radioactive Cs removal to be used as the potential candidate in Fukushima nuclear wastewater treatment. The adsorbed Cs was eluted with suitable eluent and simultaneously regenerated into the initial form for the next removal operation after rinsing with water. The adsorbent retained functionality despite several cycles during sorption–elution–regeneration operations.

Keywords: Radioactive cesium; Conjugate adsorbent; Nuclear liquid waste; Selectivity; Reuses.

1. Introduction

The Great East Japan Earthquake and accompanying tsunami have damaged the Fukushima Daiichi Nuclear Power Plant and several radioactive nuclides were released into the atmosphere. Of these nuclides, the direct release of radioactive cesium (Cs) into the environment is high and represents the largest accidental release into the ocean in history [1–3]. Radioactive Cs contamination is potentially important and also poses a serious threat to human health and environment. The Cs is of special concern due to its long half-life (30.2 y), mobility (it can be present in food and water) in the environment, and the prevalence of the great risk to the environment from the high-dosage of Cs. Moreover, cesium can easily be incorporated in terrestrial and aquatic organisms because of its chemical similarity to potassium. The radioactive Cs can enter the body and gets more or less uniformly distributed throughout the body, with higher concentration in muscle tissues and lower in bones, thereby creating an internal hazard [4–6]. Therefore, nuclear waste containing Cs needs to be treated prior to expanding to the environment.

The cleanup of radioactive Cs is very difficult due to the lack of knowledge of behaviour of ultra-trace ions that compete with the high amount of monovalent cations. Therefore, selective cesium ion separation and removal from nuclear waste is of significant interest and is a challenging task. Solvent extraction methods involving the crown ethers have shown promising Cs separation from waste solutions. A number of crown ethers have been extensively used for Cs extraction, which has a good match between the cavity of the crown ether and the crystal ionic radius of the Cs ion. There are several reports investigated involving the extraction of Cs with the 18/24-membered and crown ethers [7–9]. The crown ethers have yielded promising results for selective separation of Cs from complex water and nuclear waste solutions. However, the prohibitive cost of these compounds has been a major hurdle in their use in the large-scale process for potential applications.

There are various technologies that have been developed over the years to remove radioactive Cs from wastewater, including co-precipitation, solvent extraction, ion-exchange and adsorption processes, and solid phase extraction [10–13]. However, the co-precipitation and solvent extraction have drawbacks such as low selectivity and generation of large amounts of secondary wastes. Adsorption is one of the most popular methods and attractive processes for the treatment of cesium-bearing waste waters. This process is flexible, simple, compact, and efficient enough to achieve decontamination factors of several orders of magnitude, and does not require any toxic organic solvent [14–16]. However, the selection of the wastewater treatment methods is based on the concentration of waste contaminants and the cost of treatment. The widespread industrial use of low-cost adsorbents for wastewater treatment is strongly recommended and investigated due to their technical feasibility, engineering applicability and cost effectiveness. Therefore, many scientists have tried hard to find efficient and low-cost materials for selective decontamination of Cs containing water and low-level waste. The Prussian blue supported carbon nanotubes materials, and zeolite are used for Cs removal from water [6]. However many of these adsorbents are not reusable, and often have concomitant environment hazards.

Nanoscience and nanotechnology have gained considerable importance due to the needs and applications of nanomaterials in almost all areas of human endeavour. Nanomaterials are suitable candidates to fulfill requirements of high sensitivity and selectivity in solid-liquid phase extraction and removal of metal ions [17–19]. Due to the huge specific surface area and absence of internal diffusion resistance, nanoscale adsorbents may have superior performance for removing toxic contaminants (high sorption capacity and fast sorption kinetics) from water and waste effluents. The mesoporous inorganic silica materials have been modified with a wide variety of chemical functionalities using ligands forming a new class of nano-engineered adsorbents. Adsorbents containing different

functional ligands for the selective sorption and recovery of heavy metals [20], lanthanides [21], precious metals [22] and toxic metals [23] were reported by our research group. The organic ligand in inorganic silica surfaces by covalent bonds followed co-condensation into the inorganic framework cross-links to accessible target ions capturing with high sensitivity.

In the present study, dibenzo-24-crown-8 ether (DB24C8) immobilized onto mesoporous inorganic silica materials was investigated as a new class of adsorbent for Cs removal from radioactive waste solution in Fukushima. The preparation approach and combination of organic and inorganic materials makes it possible to take advantage of the enhanced Cs retention and ease of separation. The adsorbent has high surface area; large pore volumes implied a promising new class conjugate adsorbent for Cs removal. The functionalized crown ethers immobilized adsorbent for the effective coordination ability with Cs is the important aspect to understand the Cs- π interaction of the benzene ring with a stable complex mechanism. The main objective of this work was to develop suitable adsorbent for efficient Cs removal with high selectivity and cost-efficiency. Therefore, the present work is significant for the development of Cs separation technology. Several parameters were investigated systematically, including mesoporous material processing, characterization, adsorbent preparation, pH of the initial solution, sorption capacity, the competing ions effect, and reuse studies. The conjugate adsorbent also performed to remove the radioactive Cs containing samples to evaluate the potential practical application in Fukushima, Japan.

2. Materials and methods

2.1. Materials

All materials and chemicals were of analytical grade and used as purchased without further purification. Tetramethylorthosilicate (TMOS) and the triblock copolymers of poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) designated as F108

(EO₁₄₁PO₄₄EO₁₄₁) were obtained from Sigma–Aldrich Company Ltd. USA. The crown ether of DB24C8 was purchased from Tokyo Chemical Industry (TCI) Co. Ltd., Japan. The structure of DB24C8 is shown in **Scheme 1**. The cesium chloride (CsCl) source of Cs ion, and metal salts for the source of metal ions were purchased from Wako Pure Chemicals, Osaka, Japan. Ultra–pure water prepared with a Millipore Elix Advant 3 was used throughout this work.

2.2. Preparation of mesoporous inorganic silica monoliths and conjugate adsorbent

The F108 (EO₁₄₁PO₄₄EO₁₄₁, MW: 14,600) surfactant was used as scaffolding in preparation of inorganic silica materials. The procedure for preparation of mesoporous silica monoliths involved adding TMOS and triblock copolymers (F108) to obtain a homogenized sol–gel mixture based on the F108/TMOS mass ratio. An acidified aqueous solution was added to the mixture to quickly achieve the desired liquid crystal phase and then to promote hydrolysis of the TMOS around the liquid crystal phase assembly of the triblock copolymer surfactants. The mesoporous silica monoliths were synthesized following the reported methods [24]. In typical conditions, the composition mass ratio of F108:TMOS:HCl/H₂O was 1.4:2:1 respectively. Mesoporous silica monoliths were synthesized by using direct templating method of lyotropic liquid crystalline phase of F108 as the soft template. Homogeneous sol–gel synthesis was achieved by mixing F108/TMOS in a 200 mL beaker and then shaking at 60°C until homogeneous. The exothermic hydrolysis and condensation of TMOS occurred rapidly by addition of acidified aqueous HCl acid (at pH = 1.3) solution to this homogeneous solution. Then the methanol produced from the TMOS hydrolysis was removed by using a diaphragm vacuum pump connected to a rotary evaporator at 45°C. The organic moieties were then removed by calcination at 500°C for 6 h under the normal atmosphere. After that the material was ground properly and ready to use for immobilization

with DB24C8 ligand to prepare as new class adsorbent for Cs removal from nuclear wastewater.

The conjugate adsorbent was fabricated by direct immobilization method. The DB24C8 (50 mg) was dissolved in *N, N*-dimethylformamide (DMF) solution and then 1.0 g inorganic silica materials was added. The immobilization procedure was performed under vacuum at 45°C for 8 h stirring until the DB24C8 saturation was achieved. The DMF was removed by a vacuum connected to a rotary evaporator at 80°C and the resulting adsorbent was washed in warm water to check the stability and elution of DB24C8 from inorganic silica materials. The DB24C8 exhibited of specific functional groups for actively bonding to Cs in capturing system by complexation mechanisms because the DB24C8 embedded with inorganic silica by abundant hydroxyl groups of pore surface silicates and the heteroatoms of DB24C8 ligand. Then the materials were dried at 45°C for 6 h and grinded properly for Cs removal experiments.

2.3. Cesium removal and reuse studies

In removal systems, the conjugate adsorbent was immersed in Cs ion concentration and adjusted at specific pH values by adding of HCl or NaOH in 10 mL solutions for 1 h shaking at room temperature and amount of adsorbent used was also 10 mg. In case of pH effect evaluation, initial Cs concentration was 0.15 mM. The conjugate adsorbent was separated by filtration method and Cs concentration in before and after removal operations were analyzed by atomic absorption spectrophotometry (AAS). The batch single and multi-component sorption experiments were performed at room temperature (25°C). The amount of adsorbed Cs was calculated according to the following equations:

$$\text{Mass balance } q_e = (C_0 - C_f) V/M \text{ (mg/g)} \quad (1)$$

$$\text{and Cs sorption efficiency } E_0 = \frac{(C_0 - C_f)}{C_0} \times 100 (\%) \quad (2)$$

where V is the volume of the aqueous solution (L), and M is the weight of the adsorbent (g), E_0 is the sorption efficiency, C_0 and C_f are the initial and final concentrations of Cs ion in solution, respectively.

The effect of co-existing cations such as Na and K on Cs sorption onto the conjugate adsorbent was evaluated. The initial concentration of Cs was 0.015 mM, while the competing Na and K were varied from 0.128 to 4.35 mM. After dissolving the Na and K in the solutions, sorption experiments were performed in the same manner according to the sorption experiment.

To investigate the most efficient eluting agent, first 10 mL of 0.25 mM Cs was adsorbed on the 40 mg adsorbent. Then the adsorbed Cs onto the adsorbent was washed with deionized water and transferred into the test tube. After that the Cs elution experiments were carried out using a different concentration (0.1–0.5 M) of HCl acid. To this 2.0 mL of the eluting agent was added, and then the mixture was shaken for 5 min. The concentration of Cs released from the adsorbent into aqueous phase was analyzed by AAS. Then the conjugate adsorbent was reused for several cycles to investigate the reusability.

2.4. Analyses

The N₂ adsorption–desorption isotherms were measured using BELSORP MINI-II analyzer (JP. BEL Co. Ltd.) at 77 K. The pore size distribution was measured from the adsorption isotherms plot by using nonlocal density functional theory (NLDFT). The mesoporous silica monoliths were pre-treated at 100°C for 3 h under vacuum until the pressure was equilibrated to 10⁻³ Torr before the N₂ isothermal analysis. The specific surface area (S_{BET}) was measured by using multi-point adsorption data from the linear segment of the

N₂ adsorption isotherms using Brunauer–Emmett–Teller (BET) theory. Transmission electron microscopy (TEM) was obtained by using a JEOL (JEM–2100F) and operated at the accelerating voltage of the electron beam 200 kV. The TEM samples were prepared by dispersing the powder particles in ethanol solution using an ultrasonic bath and then dropped on copper grids. Almighty shaker (As-one, AS-1N) was used for shaking the mixture solution. The metal ion concentrations were measured by AAS (Hitachi, Z–2300). The instrument was calibrated using five standard solutions containing 0, 0.5, 1.0, 2.0 and 5.0 mg/L (for each element), and the correlation coefficient of the calibration curve was higher than 0.9999. In addition, sample solutions having complicated matrices were not used and no significant interference of matrices was observed.

2.5. Radioactive samples collection and radioactive Cs removal

In Fukushima, the radioactive Cs consists of ¹³⁴Cs and ¹³⁷Cs. However, the life time of ¹³⁴Cs and ¹³⁷Cs is ca. 2 and 30 years, respectively. Then the ¹³⁷Cs samples were collected from Japan Radioisotope Association (JRIA), Japan. The initial sample radioactivity was 3.70 MBq. Therefore, the stock solution was prepared to make low level radioactivity by adding distilled water and checking the radioactivity. The final radioactivity of the solution was 112 Bq. Also note that the pH was adjusted to 6.67 by adding of HCl and or NaOH as needed. In radioactive Cs removal operation, 10 mg of each adsorbent was immersed in 1.0 mL solution and shaken for 0.5 to 6 h. The spike different concentrations (1.03 to 3.48 mM) of K and/or Na were added to measure the selectivity by the adsorbent for evaluating the selectivity as potential candidate for radioactive ¹³⁷Cs removal in real wastewater samples. Then the solid material was separated by filtration method (0.2 μm, PTFE) and radioactivity was checked of filtrate solution (0.6 mL). The radioactivity of ¹³⁷Cs was measured by a germanium semiconductor detector (Seiko EG&G Co., Ltd.).

All experiments in this study were duplicated at least to assure the consistency and reproducibility of the results and average data was listed in this work.

3. Results and discussion

3.1. Characterization of mesoporous silica and conjugate adsorbent

The N₂ isotherms show the typical type IV adsorption behavior with a broad hysteresis loop of H₂ type along well-known sharp inflections of adsorption/desorption branches (**Fig. 1**) and adsorption branches were significantly shifted toward lower relative pressure (P/P_0). Moreover, the N₂ adsorption–desorption measurements indicate that silica materials possess good mesopore structure ordering and a relatively narrow pore size distribution. The framework porosity also indicated that the porosity within the uniform channels implied the presence of framework and textural porosity. Therefore, the mesoporous silica monoliths observed the appreciable textural parameters of specific surface area (S_{BET}), mesopore volume (V_p), and tunable pore diameters. Large pore volume, pore diameter and high surface area of the mesoporous silica monoliths samples indicate that the samples have mesoporous structure. In such direct fabrication of mesoporous adsorbent without additive coupling agents clarify the low operating cost. Such material has great advantages for fabrication of crown ether immobilized adsorbent for removal of trace Cs from wastewater. However, the surface modification method enhanced the stability of the adsorbent due to strong electrostatic interactions between heteroatoms of crown ether molecules and charged silica surfaces [**19**].

The scanning electron microscopy images of as-synthesized samples are shown in **Fig. 2(A,B)**. SEM pictures of the samples are typical for the silicate mesoporous materials and show large particle morphologies [**22,24**]. A higher magnification SEM image indicated the presence of macropores of various sizes ranging from 1 to 10 μm . The micrographs

clearly revealed that the resulting particles were almost perfectly spherical in shape. TEM images show uniform arrangement pores and continuous arrays along all directions (**Fig. 2(C,D)**) which indicate the direct interaction between the crown ethers and silica into the rigid condensed pore surfaces with retention of the ordered structures, leading to high flux and Cs ion transport at optimum pH conditions during removal operation. Moreover, the TEM image recorded perpendicular to the pore channels and showed well-organized parallel channels and clarified a hexagonally ordered array of circles, which clarified the prepared material was a typical hexagonal. After successful macrocyclic ligand immobilization onto mesoporous silica, the appreciable pores were also observed as judged from **Fig. 2 (E,F)**.

The adsorbent was fabricated by direct immobilization approach. After immobilization of DB24C8 with heteroatoms bonding, a decrease in the surface area (S_{BET}) and average pore diameter of adsorbent provided further the presence of crown ethers on the surface partially blocks the sorption of hetero-atoms as judged from **Fig. 1(b)**. The characterization also confirmed that the ability to achieve flexibility in the specific activity of the electron acceptor or donor strength of the chemically responsive DB24C8 ligand molecule may lead to easy generation and transduction of selective Cs removal by Cs- π interaction of the benzene ring of crown ether for stable complexation mechanism.

3.2. Cesium sorption

3.2.1. Effect of solution pH

The pH of solution is a significant parameter in controlling the sorption process of the metal ions. Moreover, it affects both the electrical charge on the surface of adsorbent and the speciation of metal ions in aqueous solutions. To optimize the specific pH for maximum removal efficiency, effect of pH on the Cs sorption of the adsorbent was determined. In the study, sorption of cesium was studied over a pH range of 1.0–9.0. The effect of pH of Cs

sorption onto the conjugate adsorbent is shown in **Fig. 3(A)**. Cesium sorption capacity with this adsorbent reached a maximum at pH of 5.5~9.0. The maximum sorption capacity was found at pH 7.0. Therefore, the optimum operational pH was selected as 7.0 based on the alkaline nature of the waste solution to be treated. Although the pH 9.0 was adjusted by adding NaOH, the Na concentration was neglected in this case. It has been reported that cesium ion is essentially adsorbed by specific sorption in neutral pH area by coal fly ash type adsorbent [25]. In case of ion-exchange adsorbent, high pH is favorable for monovalent Cs due to the ion-exchange competition. It is noted that ion exchange sites are mainly protonated at low pH, making them less available for cation transportation. Therefore, increasing pH values, the sites become available for cation, leading to higher sorption [26]. However, ligand supported adsorbents have specific sensitivity at a specific pH region [27].

3.2.2. *Effect of contact time*

A series of batch contact time experiments was performed to define and evaluate the optimum Cs ion sorption by the adsorbent, and the filtrate solution was checked by AAS after each fraction. Here, the initial concentration of Cs ions was 0.015 mM in 10 mL volume, and the amount of adsorbent was 10 mg. The results are also depicted in **Fig. 3(B)**. The data confirmed that Cs sorption versus time curves was single, smooth and continuous indicating monolayer sorption onto mesoporous adsorbent surfaces. The data also clarified that rapid sorption occurred during the first few minutes reaction contact time followed by slow increase to reach equilibrium. The rapid sorption is possible due to the availability of active sites to make complexation on the adsorbent surface. On the other hand, the slow sorption was observed due to the availability of active sites to make gradual sorption to reach equilibrium sorption. This kind of sorption is reported by several investigators [4,5]. It is estimated that the rapid sorption might be occurred to the external surface. However,

increasing the contact time enhances the sorption efficiency and maximum sorption was attained within 60 min. Based on these results, a shaking time of 3 h was found to be sufficient for subsequent sorption experiments to reach equilibrium when initial C_s concentration was high for the evaluation of equilibrium or maximum sorption capacity.

3.2.3. Sorption isotherms

The C_s ion distribution between the adsorbent and the C_s solution under equilibrium conditions are an important issue in the evaluation of maximum sorption capacity. Moreover, sorption isotherm is the sorption equilibrium in which the degree of interaction between the amounts of adsorbate on the adsorbent. In this connection, the practical operations require the equilibrium correlations of the experimental sorption to empirical sorption, and this can be justified by the Langmuir isotherms model. The Langmuir isotherm model was chosen to estimate the maximum sorption capacity corresponding to complete monolayer coverage on the adsorbent. The adsorbent has a finite capacity for the adsorbate, and the saturation value is reached when no further sorption can occur by the adsorbent. Therefore, Langmuir equation has been successfully applied to this sorption operation as follows [28]:

$$C_e/q_e = 1/(K_L q_m) + (1/q_m)C_e \quad (\text{linear form}) \quad (3)$$

where q_m is the maximum sorption capacity, K_L is the Langmuir sorption equilibrium constant; C_e and q_e are the concentration of the adsorbate in the equilibrated solution and the amount of adsorbed on adsorbent, respectively. The q_m and K_L are the Langmuir constants which are related to the sorption capacity and energy of sorption, respectively, and can be calculated from the intercept and slope of the linear plot, with C_e/q_e versus C_e as shown in **Fig. 4** (inset). **Fig. 4** shows that the isotherm is a regular concave curve to the equilibrium C_s

concentration axis. The data revealed that amount of Cs adsorbed increases significantly at the low concentration range and then increases gradually at high Cs concentrations. The linear fits to experimental data were obtained by the Langmuir isotherms equation. The linear plot of C_e/q_e versus C_e shows that the sorption obeys the Langmuir model for conjugate adsorbent. The Cs sorption isotherm data on conjugate adsorbent was in agreement with the Langmuir model with an excellent fit ($R^2 > 0.98$), indicating monolayer sorption. The maximum sorption capacity corresponding to complete monolayer coverage from the Langmuir model showed a mass capacity of 77.70 mg/g. However, the present conjugate adsorbent has higher maximum sorption capacity for Cs than the reported ligand immobilized adsorbent [23]. The Cs sorption is also confirmed by the STEM-EDS mapping as judged from **Fig. 5**. This could be justified by the size compatibility of the used ligand and the complexation ability of the conjugate adsorbent. It is also noted that high sorption capacity obtained on adsorbent because adsorbent has spherical nanosized cavities leading to high flux and Cs ion uptake. The obtained sorption capacities of the adsorbent are comparable with other adsorbents from the literature given in **Table 1**.

3.2.4. Effect of competing ions

The Cs sorption depends upon the competition of ion species and concentrations. A series of batch experiments was evaluated to define the specific Cs sorption by the conjugate adsorbent from aqueous solutions. Here, the solutions were prepared where the Na or K concentrations were varied from 0.13 to 4.35 mM and Cs concentration was 0.015 mM at optimum pH condition. The results are shown in **Fig. 6**. The data clarified that the Cs sorption had no adverse effect in the low concentration of Na and K ions. The results also demonstrated that the Cs sorption was greatly affected by high concentration of K ion by the adsorbent. The Cs sorption was not highly affected when the K concentration was 1.03-2.56

mM as judged from **Fig. 6(A)**. The Cs sorption was reduced of 8% when K ion existed at 17-fold (**Fig. 6(A)**) due to the Cs- π interaction of the benzene ring in crown ether. This is because of the Cs- π interaction of the benzene ring in the DB24C8. Then the conjugate adsorbent prefers Cs to K. However, the uptake percentage increases significantly as K ion decreases within the investigated concentration range. Our data indicated that within the Na concentration range of 0.22–0.43 mM, the Cs (0.015 mM) sorption by the conjugate adsorbent remained unchanged (**Fig. 6(B)**). From **Fig. 6 (B)**, uptake of Cs was quite high even the Na concentration was at 290-fold. These results indicated that the Cs sorption is affected by the presence of extremely large concentration of Na and K ions into the solution due to the competitive sorption of Na and K ions from the available complexation sites of the conjugate adsorbent. Furthermore, this is probably the close similarity in the ionic radii between Cs and K rather than Cs and Na. Therefore, K ion could compete more with Cs ion during the sorption process by the adsorbent. This is in good agreement with other adsorbents on Cs sorption about the effect of K and Na ionic concentrations [29,30]. The observed Cs sorption efficiency, even at the studied concentration of 290-fold Na ions, indicates that DB24C8 immobilized conjugate adsorbent can be efficiently utilized for removal of Cs ions from the alkaline nuclear waste.

3.3. Removal performance of radioactive Cs

In optimum experimental conditions at pH 7.0 for 1.0 mL radioactive ^{137}Cs solution, the conjugate adsorbent (10 mg each) was used to treat the low-level radioactive aqueous solution. The initial radioactivity of ^{137}Cs and decrease in the activity after several interval contact times with adsorbent is depicted in **Fig. 7(A)**. In this study, initial radioactive Cs concentration was determined to be 112 Bq. The 1.0 mL volumes of radioactive Cs were firstly immersed with the conjugate adsorbent for 0.5, 2 and 6 h. After that, the solid

adsorbent was separated by filtration and supernatants solution radioactivity were analyzed. The results clarified that the conjugate adsorbent reduced substantially the radioactivity as judged from **Fig. 7(A)**. After 0.5 h contact time, the radioactive Cs was removed 95%. Increasing the contact time up to 6 h, the radioactive concentration was completely removed. However, the short contact time was sufficient to observe the maximum performance by the adsorbent. Therefore, the radioactive Cs removal trend is different for the reported grafted ion exchange fibrous adsorbent [31]. **Fig. 7(B)** also shows the radioactive Cs removal efficiency in the presence of different concentrations of K and Na ions by the conjugate adsorbent. In the presence of K (1.03 mM), the ^{137}Cs removal efficiency was 70% as judged from **Fig. 7(B)**. Similarly, in the presence of 1.54 mM of K, the removal efficiency was determined as 64%. However, the efficiency was slightly affected by the conjugate adsorbent even in the presence of high amounts of K (2.05 mM), and the removal efficiency was 59%. In addition, the removal efficiency was 75% even in the presence of 3.48 mM of Na. This is probably due to the fact of Cs- π interaction of the benzene ring of DB24C8 ligand. Also, it was noted that conjugate adsorbent is superior to the reported adsorbents and almost completely reduced the radioactivity of its original level implying the DB24C8 immobilized adsorbents to be promising candidates for effective decontamination of ^{137}Cs contained waste effluent streams.

3.4. Elution and reuses

Elution efficiency was defined based on the ratio to the mass adsorbed onto the adsorbent and the mass desorbed from the conjugate adsorbent. Therefore, the experimental work was evaluated to see whether the adsorbent could be chemically eluted and regenerated for several cycles use. However, the low concentration of monoprotic acid (HCl) could elute the adsorbed Cs to keep maintaining the functionality of the adsorbent. The experimental data also clarified that the Cs was sufficiently eluted from the conjugate adsorbent up to 99.2%

using 0.20 M HCl. After elution, the conjugate adsorbent was simultaneously regenerated into the initial form for the next sorption operation after rinsing with water. The reuses study also was performed in seven cycles, and the sorption efficiency in each cycle was measured. The data confirmed that the Cs sorption efficiency was not significantly decreased after five cycles as judged from **Fig. 8**. This study confirmed that conjugate adsorbent could be used as a cost effective potential adsorbent for efficient radioactive Cs removal from wastewater in Fukushima.

4. Conclusions

In this study, an extensive laboratory experimental work was performed for Cs removal from radioactive waste by conjugate adsorbent in batch approach. The adsorbent was prepared based on densely direct immobilization of dibenzo-24-crown-8 ether (DB24C8) onto mesoporous silica monoliths. The solution pH played an important role and maximum sorption values were obtained at a neutral pH region. The adsorbent has relatively fast kinetics and complete within 60 min. The equilibrium data followed the Langmuir isotherm model, confirming the monolayer coverage of Cs onto conjugate adsorbent. The sorption capacity of the adsorbent towards Cs was quite high and the determined capacity was 77.70 mg/g. The conjugate adsorbent has spherical nanosized cavities with large surface area which allow an increased equilibrium sorption capacity for Cs. Even in the presence of high concentration of K and Na ions, conjugate adsorbent showed a very high sorption capacity for Cs. The adsorbed Cs was eluted with 0.20 M HCl acid and simultaneously regenerated into the initial form for next Cs sorption operations. Moreover, the adsorbent was reversible and able to be used for many cycles in sorption and regeneration operations. Then the operational costs were reduced and made the adsorbent as suitable candidate for real application. In the decontamination of radioactive Cs environmental sample, ^{137}Cs was

removed successfully from its original radioactive concentration. These encouraging results suggest that the DB24C8 immobilize conjugate adsorbent can be used efficiently for Cs removal from polluted sludge and cooling water from Fukushima Daiichi Nuclear Power Plant, Japan.

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References

- [1] T.J. Yasunari, A. Stohl, R.S. Hayano, J.F. Burkhart, S. Eckhardt, T. Yasunari, Cesium-137 deposition and contamination of Japanese soils due to the Fukushima nuclear accident, *P. Natl. Acad. Sci. USA*. 110 (2011) 7525–7528.
- [2] N. Yamaguchi, S. Eguchi, H. Fujiwara, K. Hayashi, H. Tsukada, Radiocesium and radioiodine in soil particles agitated by agricultural particles: field observation after the Fukushima nuclear accident, *Sci. Total Environ*. 425 (2012) 128–134.
- [3] M. Nakano, R.N. Yong, Overview of rehabilitation schemes for farmlands contaminated with radioactive cesium released from Fukushima power plant, *Eng. Geol*. 155 (2013) 87–93.
- [4] T. Sangvanich, V. Sukwarotwat, R.J. Wiacek, R.M. Grudzien, G.E. Fryxell, R.S. Addleman, C. Timchalk, W. Yantasee, Selective capture of cesium and thallium from

- natural waters and simulated wastes with copper ferrocyanide functionalized mesoporous silica, *J. Hazard. Mater.* 182 (2010) 225–231.
- [5] R.R. Sheha, Synthesis and characterization of magnetic hexacyanoferrate (II) polymeric nanocomposite for separation of cesium from radioactive waste solutions, *J. Colloid Interf. Sci.* 388 (2012) 21–30.
- [6] E.H. Borai, R. Harjula, L. Malinen, A. Paajanen, Efficient removal of cesium from low-level radioactive liquid waste using natural and impregnated zeolite minerals, *J. Hazard. Mater.* 172 (2009) 416–422.
- [7] M.R. Antonio, M.L. Dietz, M.P. Jensen, L. Soderholm, E.P. Horwitz, EXAFS studies of cesium complexation by dibenzo-crown ethers in tri-n-butyl phosphate, *Inorg. Chim. Acta*, 255 (1997) 13–20.
- [8] P.K. Mohapatra, D.S. Lakshmi, A. Bhattacharyya, V.K. Manchanda, Evaluation of polymer inclusion membranes containing crown ethers for selective cesium separation from nuclear waste solution, *J. Hazard. Mater.* 169 (2009) 472–479.
- [9] M.L. Dietz, E.P. Horwitz, S. Rhoads, R.A. Bartsch, J. Krzykawski, Extraction of cesium from acidic nitrate media using macrocyclic polyethers: the role of organic phase water, *Solv. Extra Ion Exch.* 14 (1996) 1–12.
- [10] D. Karamanis, P.A. Assimakopoulos, Efficiency of aluminum-pillared montmorillonite on the removal of cesium and copper from aqueous solutions, *Water Res.* 41 (2007) 1897–1906.
- [11] K. Kosaka, M. Asami, N. Kobashigawa, K. Ohkubo, H. Terada, N. Kishida, M. Akiba, Removal of radioactive iodine and cesium in water purification processes after an explosion at a nuclear power plant due to the Great East Japan Earthquake, *Water Res.* 46 (2012) 4397–4404.

- [12] V. Avramenko, S. Bratskaya, V. Zheleznov, I. Sheveleva, O. Voitenko, V. Sergienko, Colloid stable sorbents for cesium removal: Preparation and application of latex particles functionalized with transition metals ferrocyanides, *J. Hazard. Mater.* 186 (2011) 1343–1350.
- [13] A. Nilchi, R. Saberi, M. Moradib, H. Azizpourb, R. Zarghami, Adsorption of cesium on copper hexacyanoferrate–PAN composite ion exchanger from aqueous solution, *Chem. Eng. J.* 172 (2011) 572–580.
- [14] I.M. El–Naggar, E.S. Zakaria, I.M. Ali, M. Khalil, M.F. El–Shahat, Chemical studies on polyaniline titanotungstate and its uses to reduction cesium from solutions and polluted milk, *J. Environ. Radioactiv.* 112 (2012) 108–117.
- [15] C. Dwivedi, A. Kumar, K.A. Juby, M. Kumar, P.K. Wattal, P.N. Bajaj, Preparation and evaluation of alginate–assisted spherical resorcinol–formaldehyde resin beads for removal of cesium from alkaline waste, *Chem. Eng. J.* 200–202 (2012) 491–498.
- [16] Y. Park, Y.C. Lee, W.S. Shin, S.J. Choi, Removal of cobalt, strontium and cesium from radioactive laundry wastewater by ammonium molybdophosphate–polyacrylonitrile (AMP–PAN), *Chem. Eng. J.* 162 (2010) 685–695.
- [17] Y. Lin, G.E. Fryxell, H. Wu, M. Engelhard, Selective sorption of cesium using self–assembled monolayers on mesoporous supports, *Environ. Sci. Technol.* 35 (2001) 3962–3966.
- [18] Y. Park, W.S. Shin, S.J. Choi, Ammonium salt of heteropoly acid immobilized on mesoporous silica (SBA–15): An efficient ion exchanger for cesium ion, *Chem. Eng. J.* 220 (2013) 204–213.
- [19] M.R. Awual, T. Yaita, H. Shiwaku, Design a novel optical adsorbent for simultaneous ultra–trace cerium(III) detection, sorption and recovery, *Chem. Eng. J.* 228 (2013) 327–335.

- [20] M.R. Awual, M. Ismael, T. Yaita, S.A. El-Safty, H. Shiwaku, Y. Okamoto, S. Suzuki, Trace copper(II) ions detection and removal from water using novel ligand modified composite adsorbent, *Chem. Eng. J.* 222 (2013) 67–76.
- [21] M.R. Awual, T. Kobayashi, Y. Miyazaki, R. Motokawa, H. Shiwaku, S. Suzuki, Y. Okamoto, T. Yaita, Selective lanthanide sorption and mechanism using novel hybrid Lewis base (*N*-methyl-*N*-phenyl-1,10-phenanthroline-2-carboxamide) ligand modified adsorbent, *J. Hazard. Mater.* 252–253 (2013) 313–320.
- [22] M.R. Awual, M.A. Khaleque, M. Ferdows, A.M.S. Chowdhury, T. Yaita, Rapid recognition and recovery of gold(III) with functional ligand immobilized novel mesoporous adsorbent, *Microchem. J.* 110 (2013) 591–598.
- [23] M.R. Awual, S. Suzuki, T. Taguchi, H. Shiwaku, Y. Okamoto, T. Yaita, Radioactive cesium removal from nuclear wastewater by novel inorganic and conjugate adsorbents, *Chem. Eng. J.* 242 (2014) 127–135.
- [24] M.R. Awual, T. Yaita, S.A. El-Safty, H. Shiwaku, S. Suzuki, Y. Okamoto, Copper(II) ions capturing from water using ligand modified a new type mesoporous adsorbent, *Chem. Eng. J.* 221 (2013) 322–330.
- [25] R. Apak, G. Atun, K. Guclu, E. Tutem, Sorptive removal of cesium-137 and strontium-90 from water by unconventional sorbents. II—Usage of coal fly ash, *J. Nucl. Sci. Technol.* 33 (1996) 396–402.
- [26] S.M. Yakout, E. Elsherif, Batch kinetics, isotherm and thermodynamic studies of adsorption of strontium from aqueous solutions onto low cost rice-straw based carbons, *Carbon – Sci. Technol.* 1 (2010) 144–153.
- [27] M.R. Awual, M. Ismael, T. Yaita, Efficient detection and extraction of cobalt(II) from lithium ion batteries and wastewater by novel composite adsorbent, *Sensor. Actuat. B* 191 (2014) 9– 18.

- [28] I. Langmuir, The constitution and fundamental properties of solids and liquids, *J. Am. Chem. Soc.* 38 (1916) 2221–2295.
- [29] A.K. Vipin, B. Hu, B. Fugetsu, Prussian blue caged in alginate/calcium beads as adsorbents for removal of cesium ions from contaminated water, *J. Hazard. Mater.* 258–259 (2013) 93– 101.
- [30] H. Long, P. Wu, N. Zhu, Evaluation of Cs⁺ removal from aqueous solution by adsorption on ethylamine–modified montmorillonite, *Chem. Eng. J.* 225 (2013) 237–244.
- [31] A. Iwanade, N. Kasai, H. Hoshina, Y. Ueki, S. Saiki, N. Seko, Hybrid grafted ion exchanger for decontamination of radioactive cesium in Fukushima Prefecture and other contaminated areas, *J. Radioanal. Nucl. Chem.* 293 (2012) 703–709.

Figure Captions

Fig. 1. N₂ adsorption/desorption isotherms at 77 K (a) high ordered inorganic silica materials synthesized by using direct templating method and (b) novel conjugate adsorbent with the difference of high surface areas and large pore sizes and volumes.

Fig. 2. SEM images of the mesoporous silica prepared by instant direct-templating method (A, B); TEM images representative of ordered nanostructures along with uniformly arranged pores in all direction (C, D) and STEM images of conjugate adsorbent (E, F).

Fig. 3. (A) Effect of solution pH for Cs sorption by conjugate adsorbent. The equilibrated individually at different pH area with 0.15 mM of Cs ions at 25°C in 10 mL volume for 1 h contact time; (B) effect of contact time in the evaluation of sorption efficiency. Initial Cs ions concentration was 0.015 mM in 10 mL volume, and the amount of adsorbent was 10 mg each. The RSD value was ~4.0%.

Fig. 4. Langmuir sorption isotherms of Cs ions and the linear form of the Langmuir plot (initial Cs ion concentration range 0.038 – 0.75 mM; solution pH 7.0; dose 10 mg; solution volume 10 mL and contact time 3 h).

Fig. 5. STEM image (A) and EDS mapping (B-D) of conjugate adsorbent after sorption of Cs; (E) the EDS analysis demonstrated the presence of Si, O and Cs in the conjugate adsorbent compositions with Cs sorption.

Fig. 6. Evaluation of Cs selectivity by the conjugate adsorbent in the presence of K and Na ions. The Cs selectivity evaluated in the presence of K (A) and Na (B). The Cs concentration

was 0.015 mM in fixed while the K and Na concentration was varied from 0.22 to 4.35 mM at pH 7.0.

Fig. 7. The ^{137}Cs removal performances by prepared conjugate adsorbent (A) and ^{137}Cs removal efficiency in the presence of K/Na (B) (Radioactive ^{137}Cs concentration was 112 Bq. while the K concentration was 1.02-2.05 mM and Na concentration was 3.48 mM).

Fig. 8. Evaluation of the efficiency changes in the sorption properties of 0.015 mM of Cs by using 20 mg of conjugate adsorbent after seven sorption–elution–regeneration/reuse cycles. The RSD values were $\sim 3.5\%$.

Table 1

Comparison of sorption capacities towards Cs by using various adsorbent materials

Used adsorbent materials	Capacity (mg/g)	References
Prussian Blue	25,52	[4]
CHCF–PAN composite	12.5	[13]
AMP–PAN	81.31	[16]
NH ₄ PMA	97.23	[18]
Inorganic adsorbent	27.40	[23]
Conjugate adsorbent	50.23	[23]
CNT–reinforced PB–encapsulated beads	142.85	[29]
Conjugate adsorbent	77.70	This study

Fig. 1.

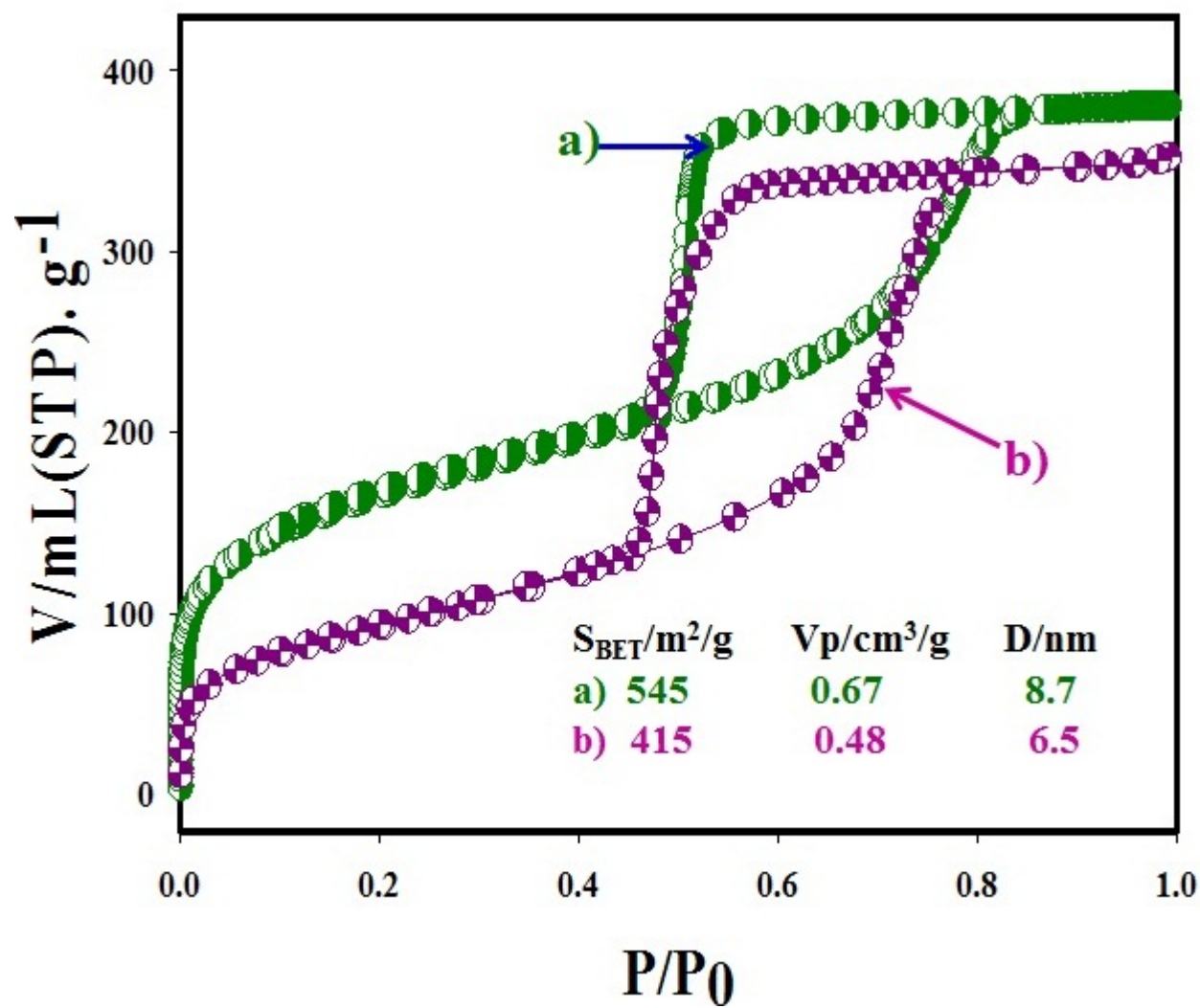


Fig. 2.

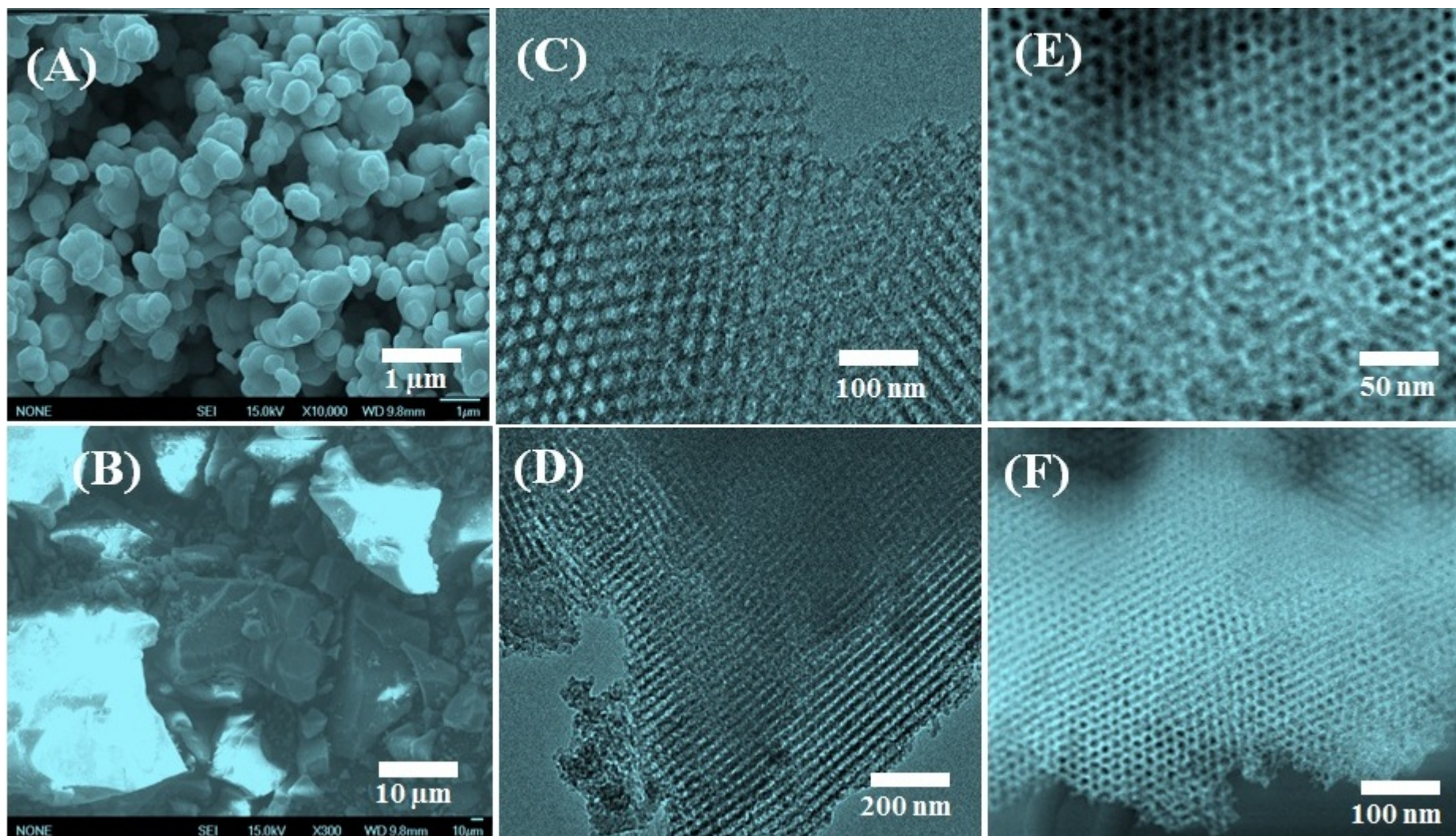


Fig. 3.

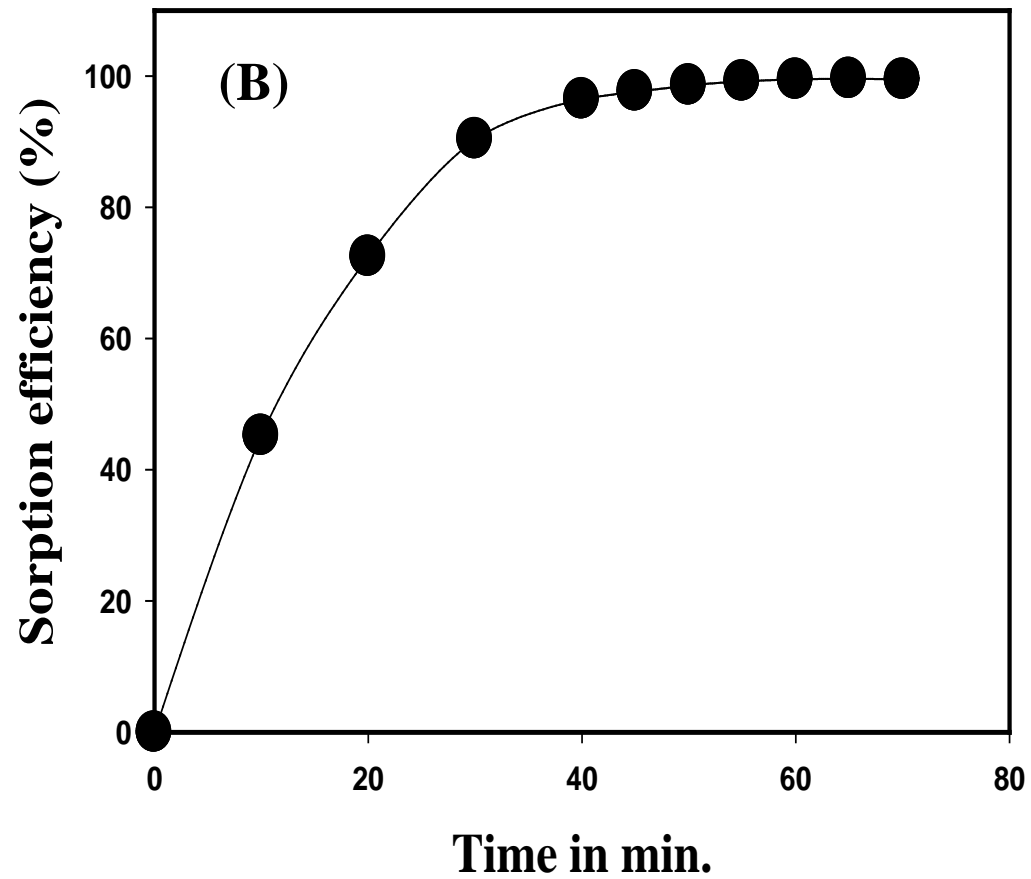
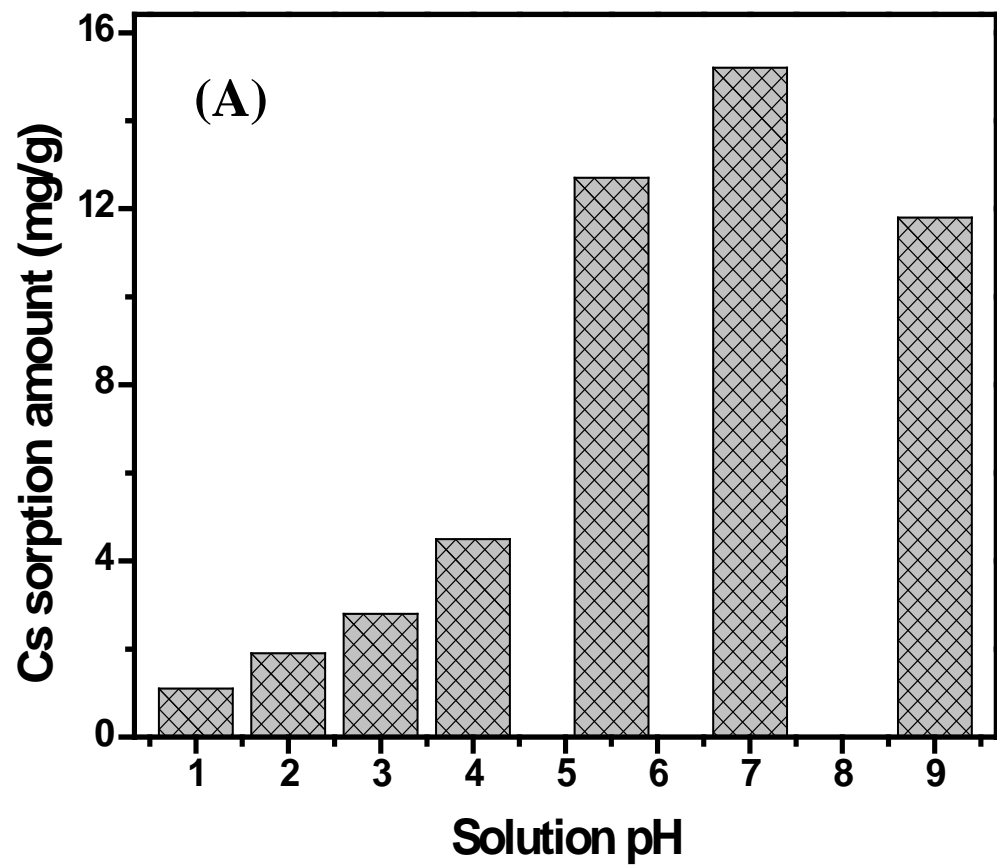


Fig. 4.

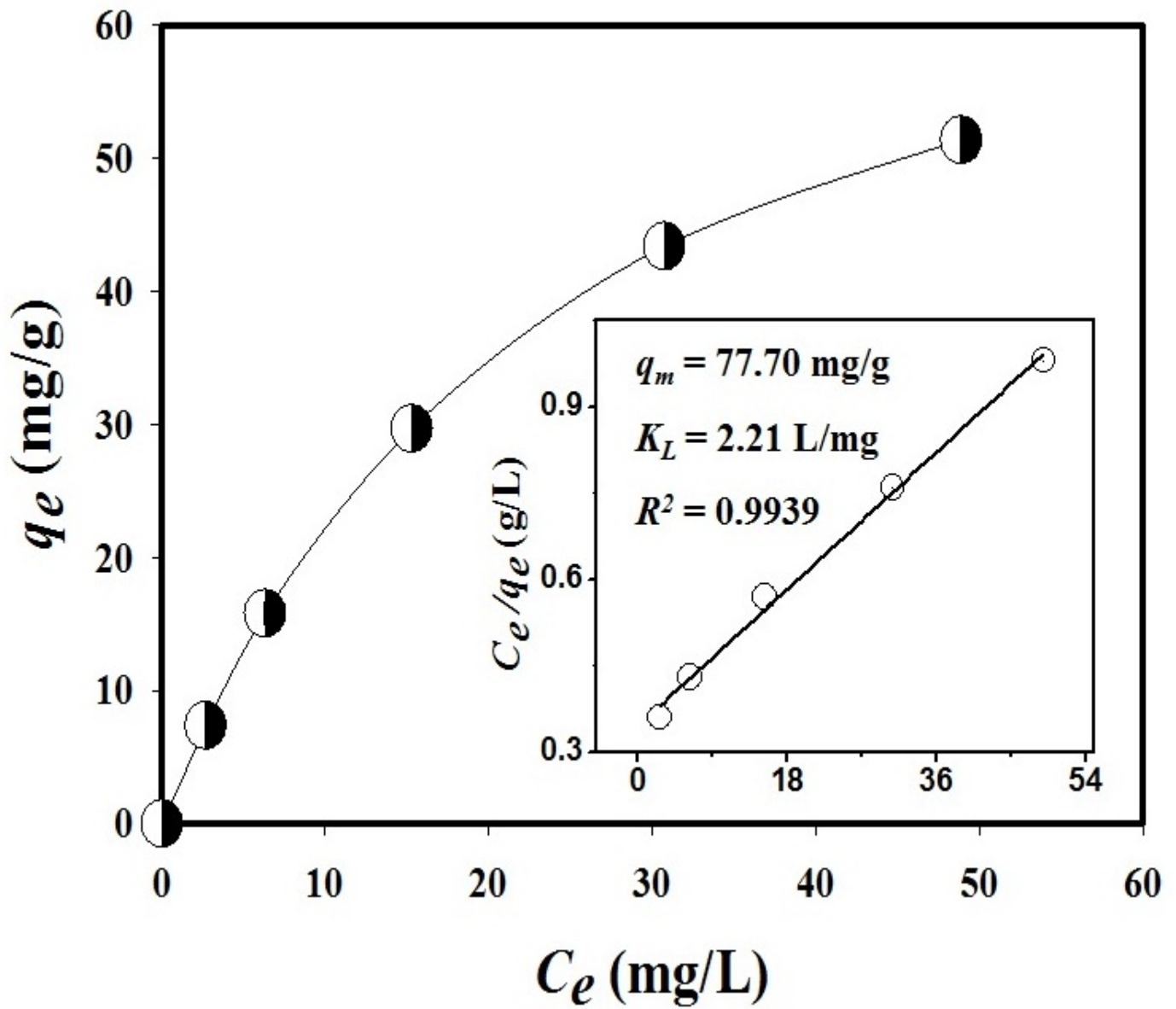


Fig. 5.

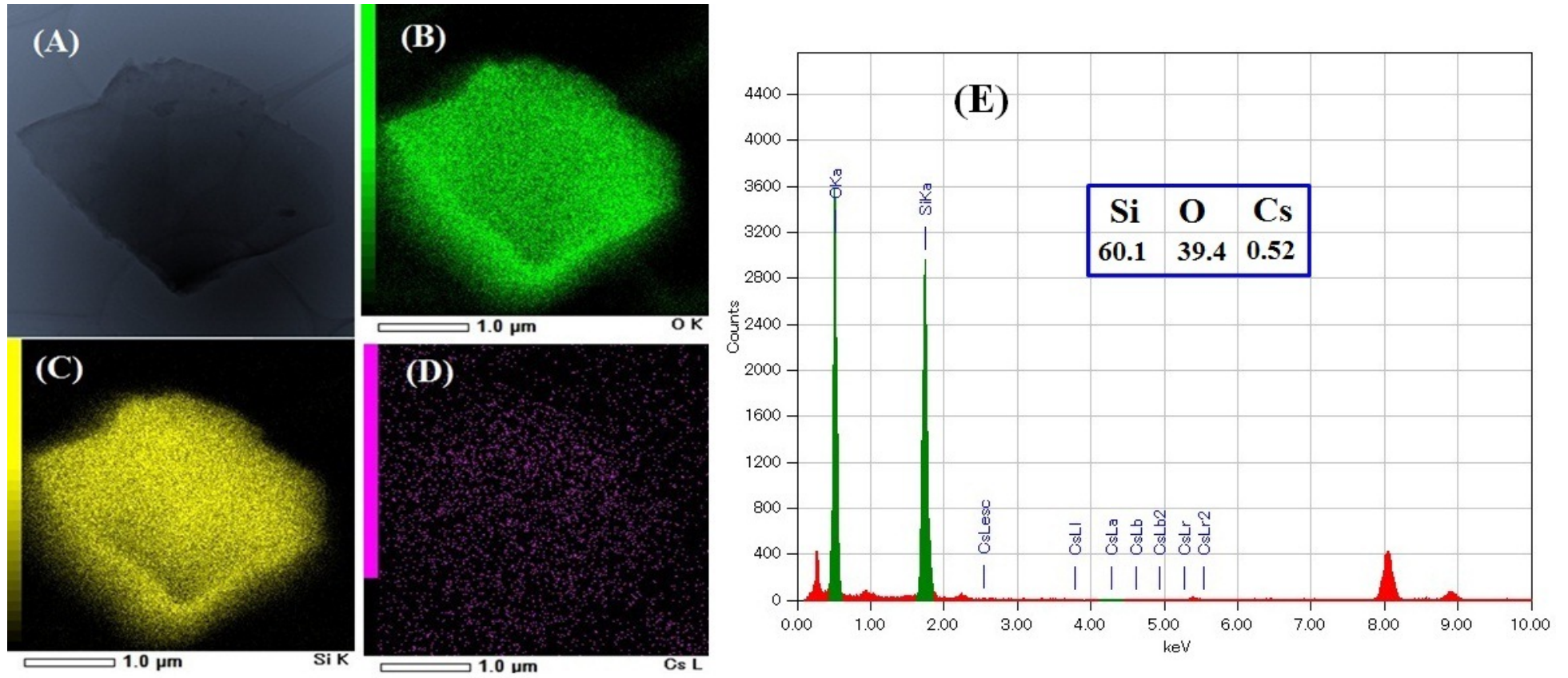


Fig. 6.

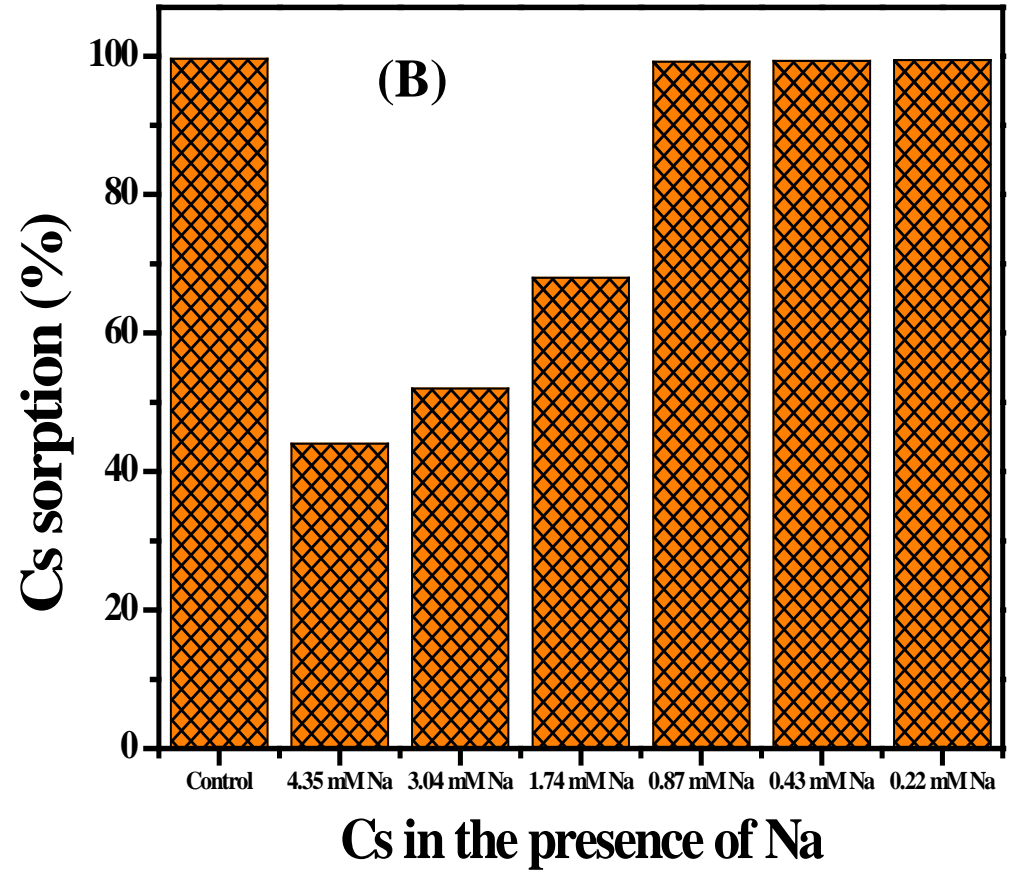
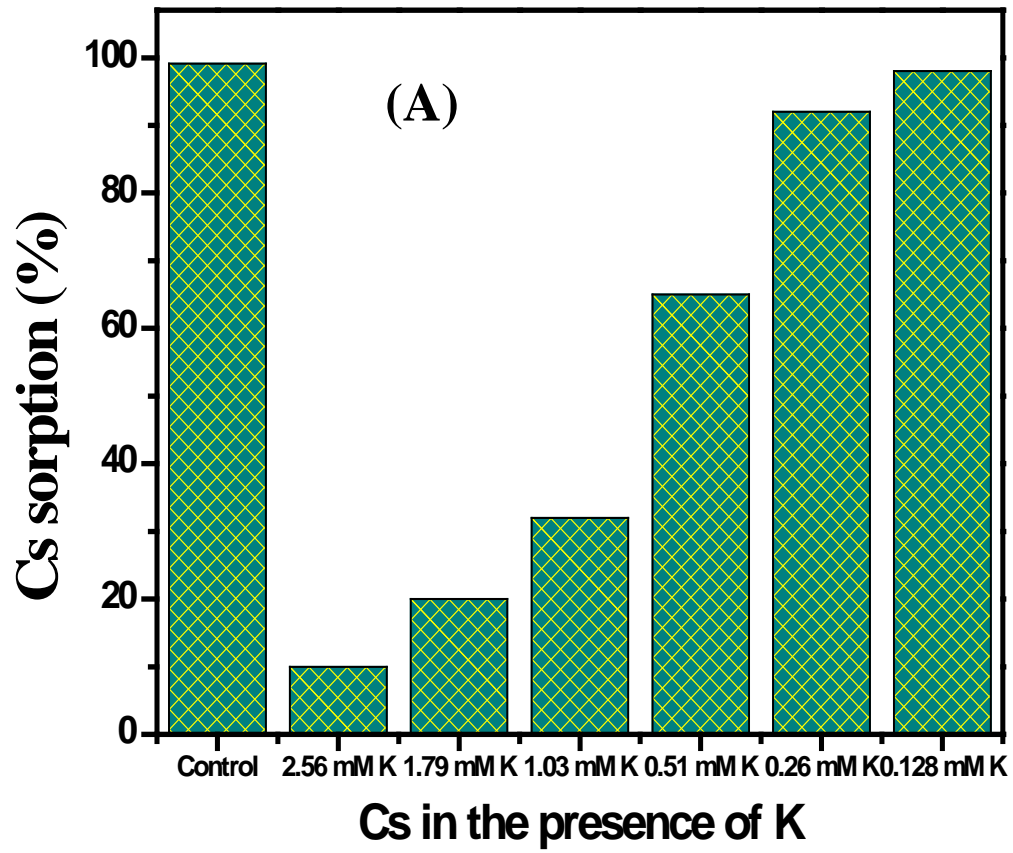


Fig. 7.

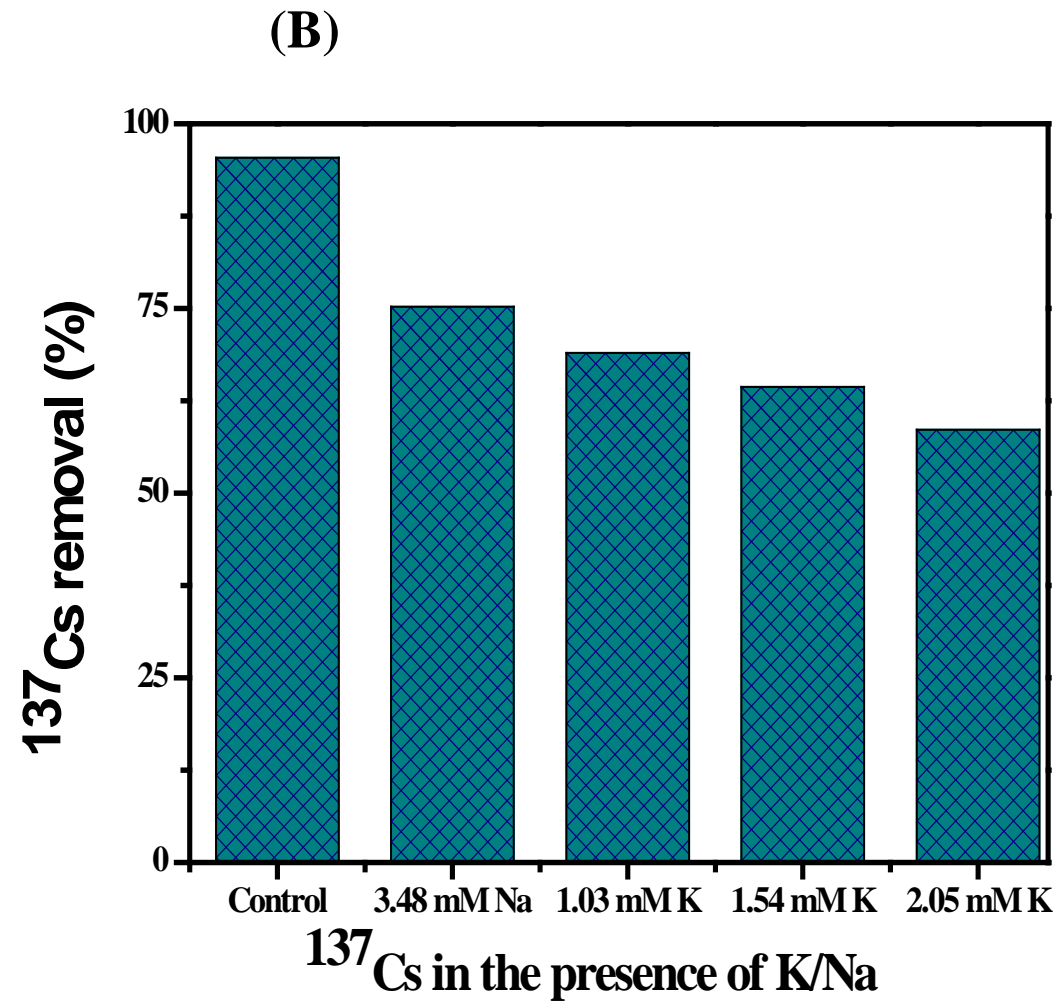
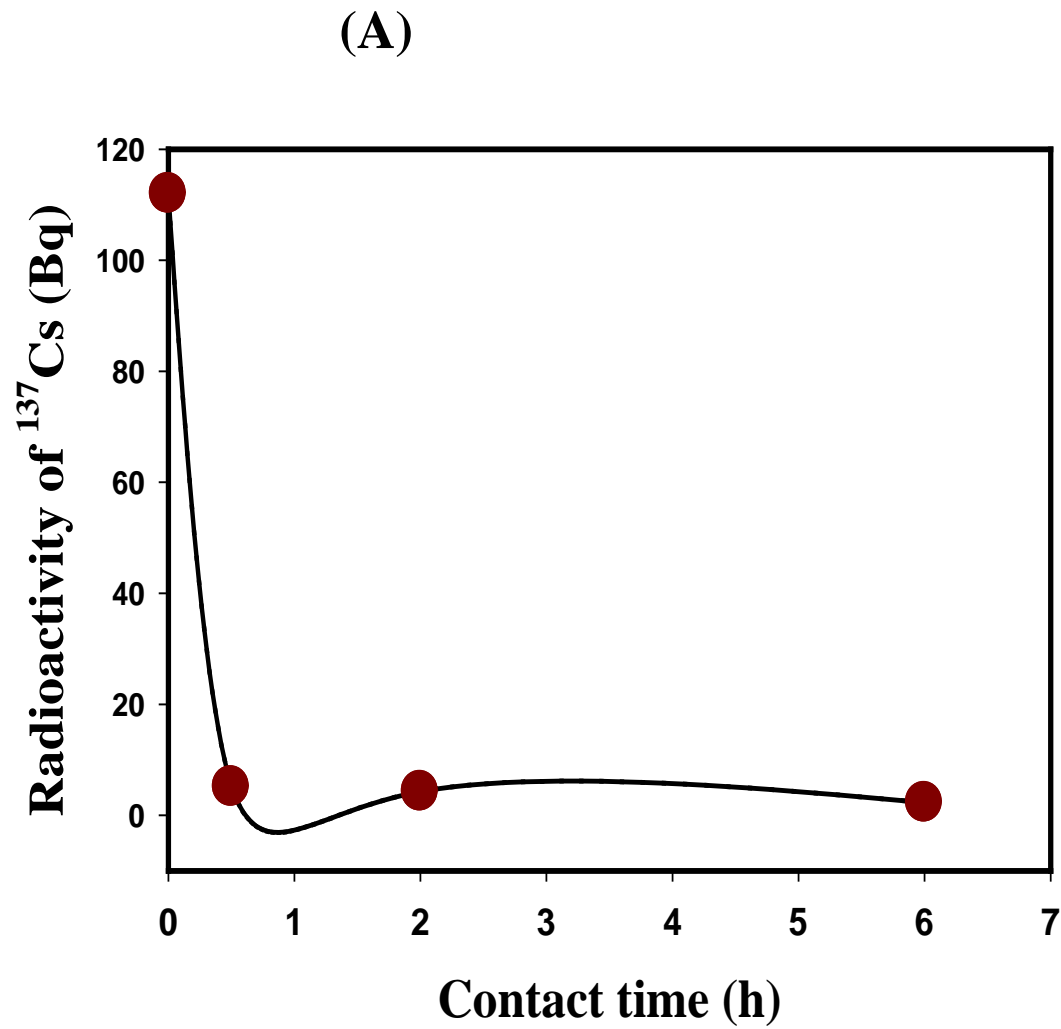
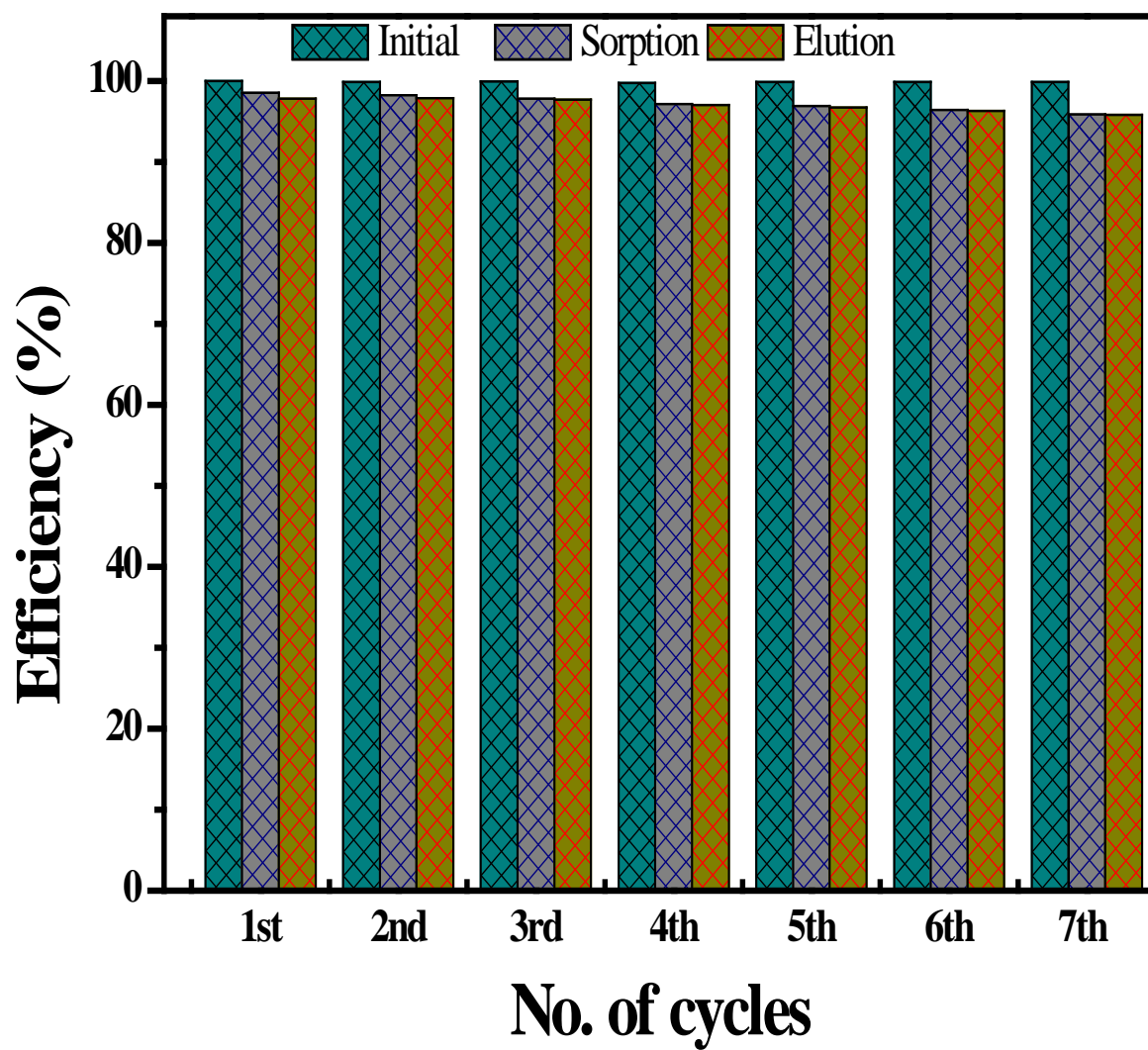
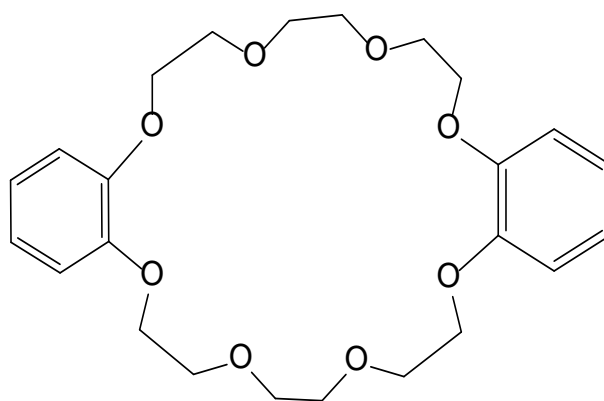


Fig. 8.





Scheme 1. The structure of macrocyclic ligand of dibenzo-24-crown-8 ether (DB24C8).