Morphology and adsorption of chromium ion on uranium 1,2,4,5-benzenetetracarboxylic acid metal organic framework (MOF)

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Abstract

In this paper, we report the synthesis of metal organic framework of uranium 1,2,4,5-benzenetetracarboxylic acid (U-H_4btec MOF) by solvothermal method. The obtained MOF was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction spectroscopy (XRD), energy dispersive spectroscopy (EDS), thermogravimetric and differential thermosgravimetric analysis (TGA/DTA). The morphology of the uranium 1,2,4,5-benzenetetracarboxylic acid MOF observed by SEM, revealed the presence of flaky porous structure. Adsorption of Cr^{3+} from aqueous solution onto the uranium 1,2,4,5-benzenetetracarboxylic acid MOF was systematically studied. Langmuir and Freundlich adsorption isotherms were applied to determine the adsorption capacity of the MOF to form a monolayer. Kinetic determination of the adsorption of Cr^{3+} suggested both chemisorption and physisorption probably due to the presence of carbonyl groups within the MOF and its porous structure.

Keywords: adsorption, physisorption, metal organic frameworks; 1,2,4,5-benzenetetracarboxylic acid, uranyl acetate dehydrate, SEM.

Available online at the Journal website: http://www.ache.org.rs/HI/

Metal organic frameworks (MOFs) are two or three-dimensional (3-D) coordination (polymers) of metal ions and organic ligands [1]. The design and synthesis of MOFs are receiving great attention because of their architecture, topology, and potential applications [2]. MOFs are potential adsorbents due to their porous structure with high specific surface area; they can also play an important role in the area of catalysis and separation [3]. As adsorbents, metal-organic frameworks have been used for hydrogen storage [4–8], gas separation and purification [9], and adsorption of volatile organic compounds [10].

Different approaches are used to synthesize MOFs, such as under solvothermal conditions, employing multidental ligands capable of binding to a metal ion to form porous complexes of supramolecular structures [3,11]. Thus, a variety of organic ligands, metal ions, and solvent systems is explored for the preparation of numerous MOFs of exotic architectures as reported in the literature [12]. The supermolecular structure is maintained together by different interactions, such as metal-to-ligand π bonding, π–π interactions or others.

Researchers have used 1,2,4,5-benzenetetra-carboxylate anion as a ligand in different study. For instance, thin films of organic–inorganic hybrid materials have been grown by the atomic layer deposition technique [13]. Lanthanide ions were used to prepare lanthanide-containing coordination polymers with 1,2,4,5-benzenetetracarboxylate acid (=H_4btec); the compounds showed 3-D and their potential porosities were estimated by a computational method to be in the range of 1281 to 836 $m^2\,g^{-1}$ [14]. Several metals have been used to prepare MOFs, such as Mn, La, Ag, Co, Cu, Cr, Fe and Zn for instance. Liu *et al.* [15] prepared 3-D material of H_4btec anion with magnesium.

However, as far as we know, uranium 1,2,4,5-benzenetetracarboxylic acid has not been synthesised for adsorption of chromium. Therefore, in this work, we report the synthesis of uranium 1,2,4,5-benzenetetracarboxylic acid (U-H_4btec), MOF from uranyl acetate and its characterization by scanning electron microscope, transmission electron microscope, x-ray diffraction spectroscopy, Fourier transform infrared spectroscopy and thermogravimetric analysis. The uranium MOF was used as a substrate for the adsorption of chromium ions in aqueous solution.

EXPERIMENTAL

Materials

1,2,4,5-benzenetetracarboxylate acid, uranyl acetate dihydrate, and *N,N*-dimethylformamide (DMF) were purchased from Merck. All were used as-received without further purification.

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Preparation

The metal ion and H₄btec were dissolved in DMF and transferred to a round bottom flask. The mixture was then refluxed at 70 °C for 2 h. The resulting solution was cooled at room temperature. The solution was then centrifuged for 30 min at 3000 rpm, and decanted. The solid residue was washed with 20 mL DMF and centrifuged again for 30 min and decanted. After centrifugation, the residue was oven dried for 4 h at 100 °C.

Characterization

The metal organic framework was characterized by FT-IR, TGA, FE-SEM, HR-TEM, EDS and XRD. IR spectra were recorded using Perkin–Elmer Spectrum 400 FT--IR/FT-NIR spectrometer in the range of 400–4000 cm^{-1}. TGA was carried out with a heating rate of 10 °C/min using STA 6000 thermal analyser Perkin–Elmer. The surface morphology measurement was recorded with a JEOL 7500F field emission scanning electron microscope (SEM) and was coupled to an EDS analyser. The HR-TEM image was obtained by CM 200 electron microscope operated at 100 kV. Powder X-ray diffraction (PXRD) patterns were collected with Bruker Kα1 radiation of wavelength λ = 1.540598 Å and Kα2 radiation of wavelength λ = 1.544426 Å. Scan speed of 1 s/step and step size of 0.03°.

Determination of Cr³⁺

The concentrations of chromium ions in solutions before and after equilibrium were determined by AA--7000 atomic absorption spectrometer-auto sampler. The absorption parameters are given in the Table 1.

Adsorption experiment of Cr³⁺ by U-H₄btec MOF

Batch adsorption experiments were performed by contacting 0.01 g of Uranium H₄btec (U-H₄btec) MOF powder with 15 mL of the aqueous solution of different initial concentrations of CrCl₃·6H₂O at pH 7.2. The experiments were performed on an orbital shaker for a period of 10, 20, 30, 40, 50, and 60 min at 150 rpm in sealed 50 mL vessels. The remaining concentration of Cr³⁺ in each sample after adsorption at different time intervals was determined by atomic absorption spectroscopy after centrifugation. The Cr³⁺ concentration retained in the adsorbent phase was calculated according to:

$$q_e = \frac{V(C_i - C_e)}{W} \tag{1}$$

where C_i and C_e are the initial and equilibrium concentrations (mg/L) of Cr^{3+} solution, respectively; V is the volume (L); and W is the mass (g) of the adsorbent.

RESULTS AND DISCUSSION

The MOF of the prepared material is built on uranium cations and 1,2,4,5-benzenetetracarboxylate anions. In addition to the cation-anion interactions, the MOF structure is probably stabilized by π–π stacking interactions within the U-H₄btec system. The cation––anion and π–πinteractions network lead to 3-D channels. The channels are an important honeycomb-like (zeolite-like) which can house different kind of matters.

FT-IR analysis

The FT-IR spectrum of U-H₄btec is shown in Fig. 1. The broad band that appeared around 3402 cm^{-1} can be assigned to be the O–H vibration due to the presence of humidity and the unreacted carboxylic acid groups. The C–H bond vibration of aromatic ring appeared at 2999 cm^{-1} and the C=O at 1746 cm^{-1}. The absorption band between 1589 and 1366 cm^{-1} can be assigned to carbon-carbon stretching vibrations in the aromatic ring of H₄btec. FT-IR spectra of the compounds feature absorptions of the MOF below 920 cm^{-1} may be attributed to the bond between uranium and oxygen, as observed by Kim *et al.* [16].

TGA analysis

The TGA and DTG plots of U-H₄btec MOF are presented in Fig. 2. From the DTG plot, the thermal decomposition of U-H₄btec appeared to be a complex process involving a large number of chemical reactions with three main steps of mass loss. The first mass loss around 70 °C can be most probably related to the release of moisture (12.3%). The next two main steps are probably related to organic volatiles, they occurred around 130 and 440 °C. The other small steps occurred in between 130 and 440 °C and after. The observation of the TGA plot permit to envisage a possible U-H₄btec MOF decomposition beyond the setting. Unfortunatly, the TGA instrument used could not allow temperature above 900 °C.

XRD analysis

The XRD pattern of U-H₄btec MOF is presented in Fig. 3. The pattern showed three prominent peaks at 2θ 6.20, 8.09 and 10.34°. Similar pattern has been reported by Kazy *et al.* [17]. The fourth peak, with low intensity appeared at 2θ 18.59°.

Table 1. Absorption parameters for the adsorption of chromium ions unto uranium MOF

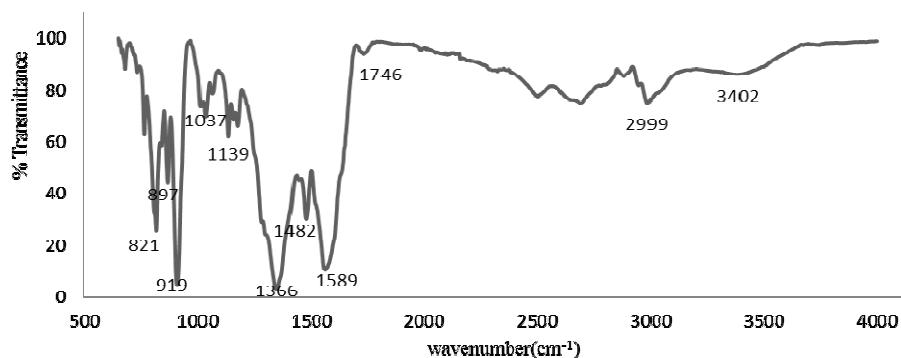| Parameter	Lamp current mA	λ nm	Slit width nm	Lamp mode	Fuel gas flow rate, L/min	Support gas flow rate, L/min	Flame type	Burner height mm
Value	10	357.9	0.7	BGC-D2	2.8	15.0	Air-C₂H₂	9.0

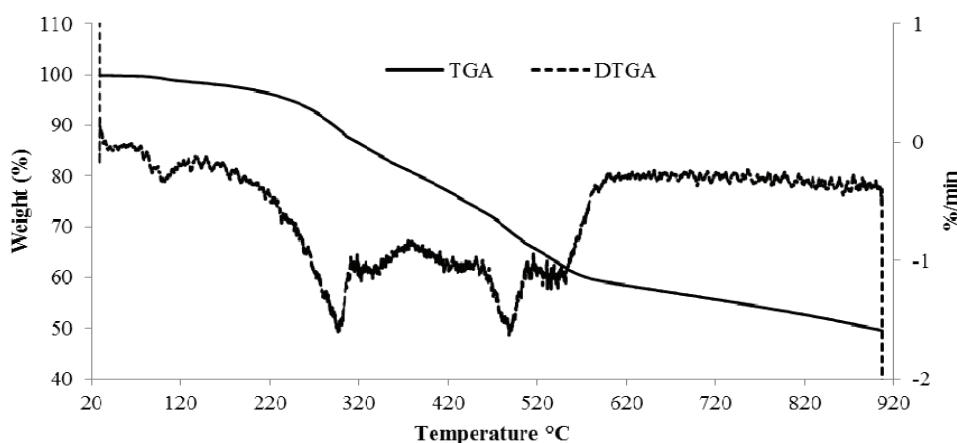Fig. 1. FTIR spectrum for U-H$_4$btec.
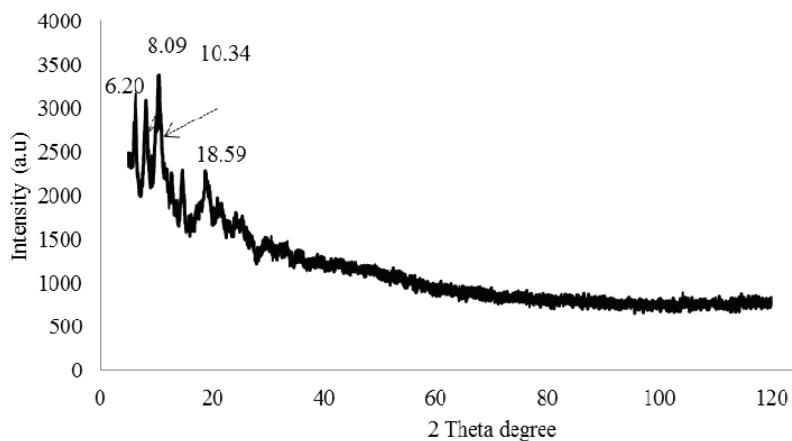

Fig. 2. TGA and DTG of U- H$_4$btec MOF.

Fig. 3. XRD spectrum for Uranium pyromellitic at room temperature.

SEM and EDS analysis

The scanning electron microscopy (SEM) image of U-H$_4$btec MOF is shown in Fig. 4. The visual observation of the SEM image did not reveal specific shapes, such as rod or stick but, showed the morphology of a porous and flaky material. The flaky structure resembling to a bunch of petals is likely to play an important role if the MOF has to be used as adsorbent. It is possible that the flaky structure of this MOF was strongly influenced by the properties of uranium. The EDS spectrum (Fig. 5)

showed clearly the presence of uranium in the structure of the MOF.

TEM Analysis

Transmission electron microscopy (TEM) analysis was conducted to study the internal morphology of synthesized U-H$_4$btec MOF. The TEM image of uranium 1,2,4,5-benzene tetracarboxylic acid MOF obtained is presented in Fig. 6. TEM result suggested the existence of U-H$_4$btec MOF in the form of pellets with particles
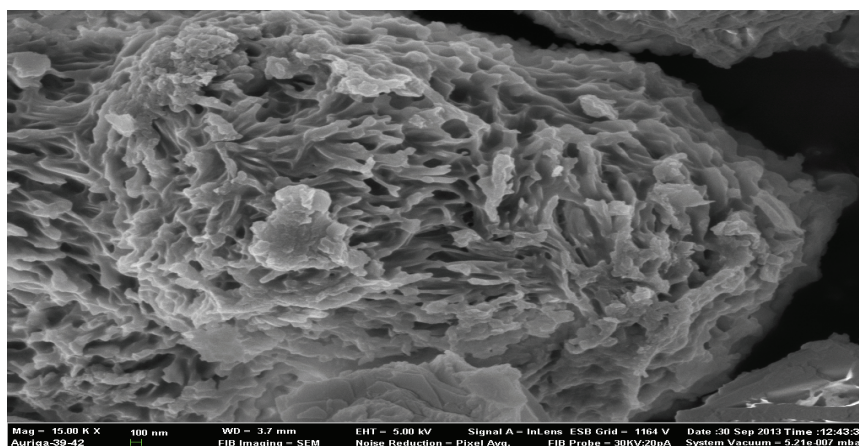
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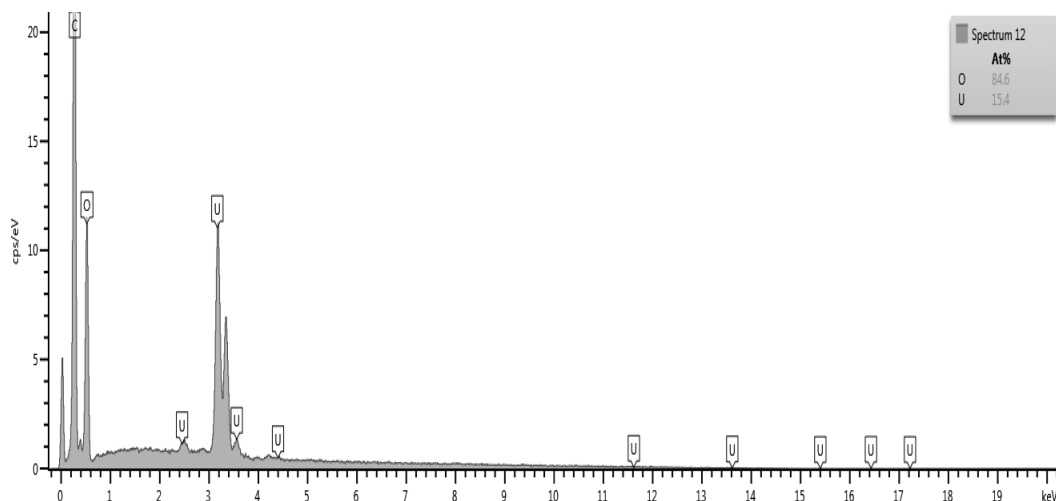*Fig. 4. SEM image for U-H$_4$btec MOF.*

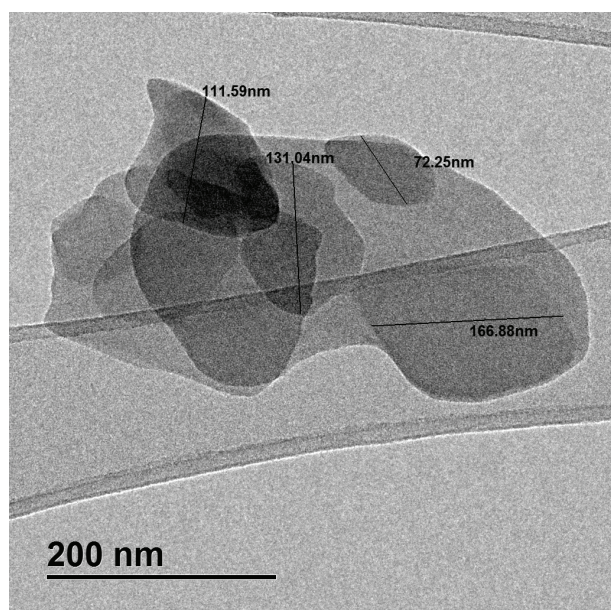
Fig. 5. EDS analysis.

Fig. 6. TEM image for U-H$_4$btec MOF.

diameter varying between 72.25 and 166.88 nm. The typical TEM image clearly confirmed the flaky and porous structure of the U-H$_4$btec framework which is in accordance with the SEM result.

Adsorption results

Adsorption was conducted using a batch setup and chromium ions were determined using atomic absorption specroscopy (with r^2 = 0.9999). The Langmuir and Freundlich isotherms were used to assess the adsorption behaviour of U-H$_4$btec MOF. The kinetics of adsorption was investigated by means of contact time, pseudo-first, and pseudo-second order reaction, in order to possibly explain the sorption mechanism, such as mass transfer and/or chemical reaction.

Effect of contact time

Time is one of the prime factors determining the adsorption behaviour of a system. Contact time was used in order to understanding the amount of Cr^{3+} adsorbed at various time intervals by a fixed amount of

the adsorbent and to monitor the equilibrium. Results (Fig. 7) showed that for the five different concentrations, equilibrium was achieved after about 30 min. The general adsorption trend could be described as: sharp increase of U-H$_4$btec uptake during the first 30 min and then equilibrium. All the plots, however, have features that suggest a cover up step before equilibrium.

Effect of concentration

The effect of initial concentration in the range of 20 to 100 mg/L on adsorption is presented in Fig. 8. Result showed that with the same amount of adsorbent, the concentration of Cr^{3+} adsorbed increased with the concentration of the initial solution. This fact can be explained by the mass transfer of Cr^{3+} and pressure onto the inner adsorption sites of the adsorbent.

Pseudo first and pseudo second order reaction

Plots of pseudo first and pseudo second order are shown in Figs. 9 and 10. They had high r^2 (from 0.8743 to 0.997) meaning that adsorption probably underwent physisorption and chemisorption processes [18]. This can be explain by the lone pair electron on oxygen

atoms (of the carboxylic moiety, behaving like a ligand) that could be responsible of a bond between the adsorbent and Cr^{3+}, possible π-π electron donor-acceptor interactions between the aromatic rings moiety of the adsorbent (H$_4$btec) and Cr^{3+}, and the presence of pores in the 3-D structure the MOF which could have trapped the adsorbate.

Adsorption isotherms

Langmuir and Freundlich isotherms (linear plots) were used to study the adsorption of Cr^{3+} by U-H$_4$btec MOF and results are presented in Figs. 11 and 12. The Langmuir model advocate for equality of affinity between adsorption sites-adsorbate and that adsorption at one site does not affect adsorption at an adjacent site on monolayer surfaces [19,20]. The Freundlich model, however, describes the equilibrium on heterogeneous systems and does not assume monolayer capacity [19,21]. Correlation coefficients (r^2) were used to estimate the best fit isotherm model for the adsorption of Cr^{3+}. r^2 values of the two models (Langmuir and Freundlich) are almost in the same range (similar), suggesting that Cr^{3+} were adsorbed on
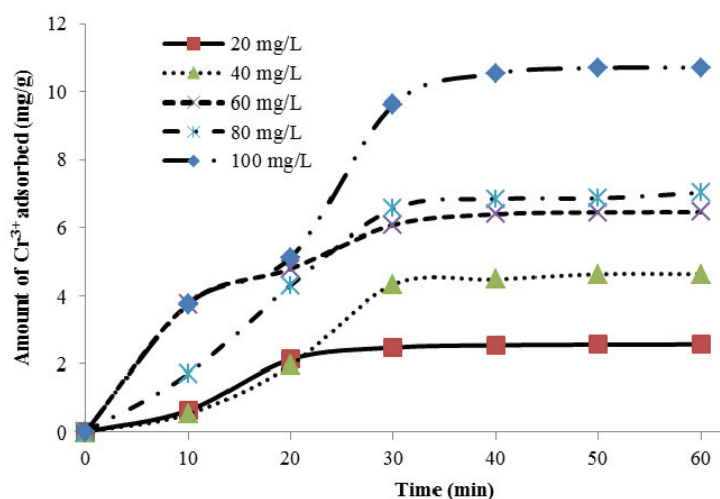

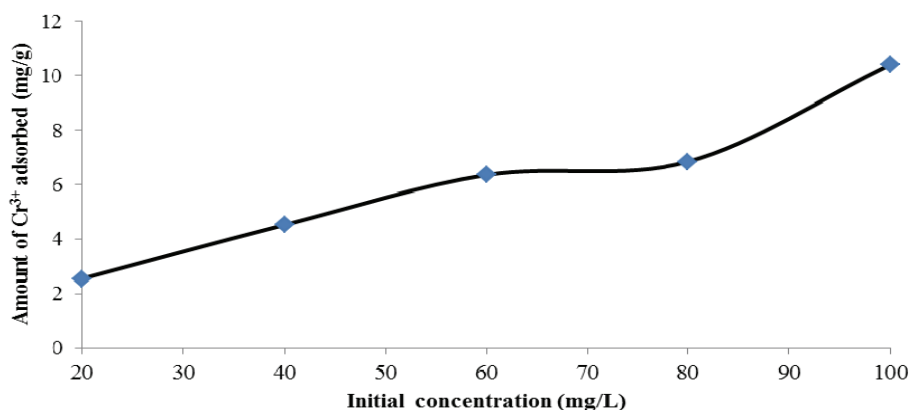*Fig. 7. Effect of time on adsorption.*

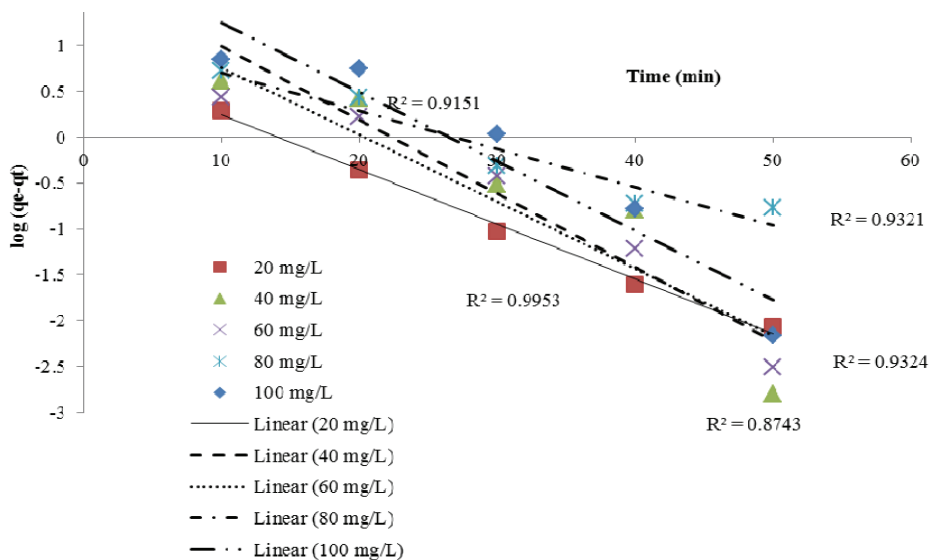*Fig. 8. Effect of Initial concentration of chroimium ions.*

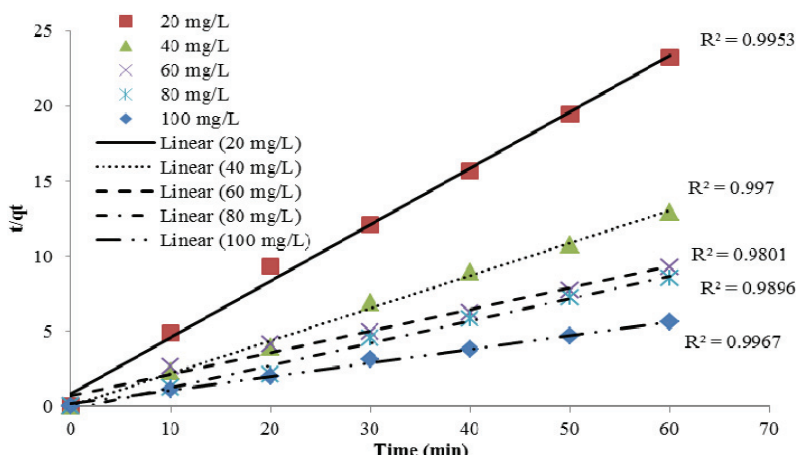Fig. 9. Pseudo first order plot of adsorption of chromium ion.

Fig. 10. Pseudo second order plot for the adsorption of chromium ions.
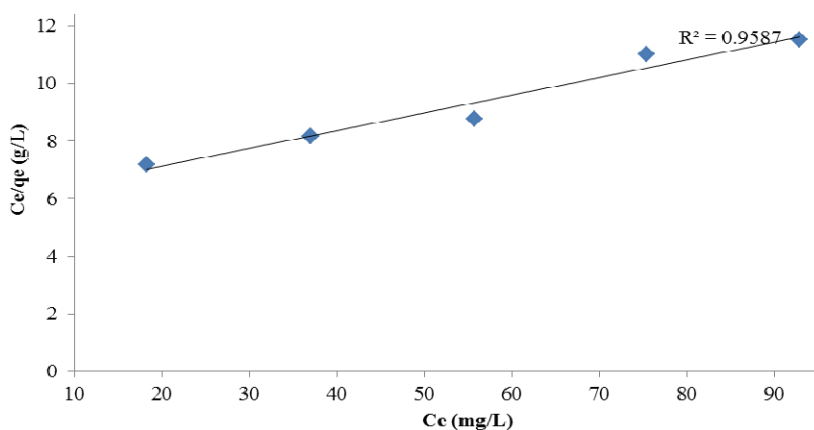

Fig. 11. Langmuir isotherm for the adsorption of chromium ions.

the surface (monolayer) and the inner sites (multilayer system) of the adsorbent. This implication should not surprise since the adsorbent (MOF) is assumed to be a three-dimensional system. Therefore, Cr^{3+} with its 75.5

pm radius size could have penetrated the U-H_4btec pores and be adsorbed by the inner adsorption sites.
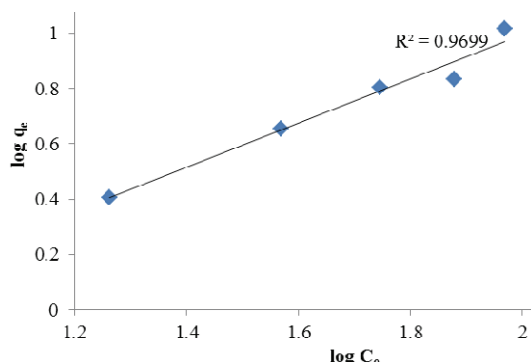
Fig. 12. Freundlich Isotherm for the adsorption of chromium ions on uranium MOF.

CONCLUSION

This work presented the synthesis of uranium 1,2,4,5-benzene tetracarboxylic acid metal organic framework by solvothermal method. Unlike many other results (rod and stick shapes), the SEM characterization of U-H$_4$btec MOF showed a flaky and porous morphology of the material. Used as adsorbent, the U-H4btec MOF showed promising adsorption properties with equilibrium reached during the first 30 min. It was observed that the Cr^{3+} uptake increased with the concentration of the initial solution and adsorption could have followed chemisorption and physisorption. Also, isotherms (Langmuir and Freundlich) suggested monolayer and multilayer systems.

Acknowledgement

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IZVOD

MORFOLOGIJA I ADSORPCIJA JONA HROMA NA METAL–ORGANSKOM OKVIRU (MOF) URAN–1,2,4,5-BENZEN-TETRAKARBOKSILNA KISELINA

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(Naučni rad)

U ovom radu pokazana je sinteza metalnog organskog okvira (MOF) uranijum 1,2,4,5-benzentetrakarboksilne kiseline (U-H4btec MOF) primenom metode termalnog rastvaranja. Izvršena je karakterizacija dobijenog MOF primenom infracrvene spektroskopije sa Furijeovom transformacijom (FTIR), skenirajuće electronske mikroskopije (SEM), transmisione elektronske mikroskopije (TEM), difrakcije X-zraka (XRD), spektroskopije dispergovane energije (EDS) i termogravimetrijske i diferencijalne termogravimetrijske analize (TGA/DTA). Morfologija MOF uranijum 1,2,4,5-benzentetrakarboksilne kiseline analizirana pomoću SEM pokazuje prisustvo lisnate porozne strukture. Adsorpcija Cr^{3+} iz vodenog rastvora na MOF uranijum 1,2,4,5-benzentetrakarboksilnu kiselinu je sistematski ispitana. Langmuir i Freundlich adsorpcione izoterme su primenjene za određivanje adsorpcionog kapaciteta MOF za formiranje monosloja. Kinetičko određivanje adsorpcije Cr^{3+} ukazuje kako na proces hemisorpcije tako i fizisorpcije, verovatno zbog prisustva karbonilne grupe u okviru MOF i njegove porozne strukture.

Ključne reči: Adsorpcija • Fiziosorpcija • Metalni organski okvir • 1,2,4,5-Benzen-tetrakarboksilna kiselina • Uranil acetat dehidrat • SEM