Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2016, Article ID 7803480, 10 pages
http://dx.doi.org/10.1155/2016/7803480

Research Article

Hydrothermal Synthesis, Characterization, and *In Vitro* Drug Adsorption Studies of Some Nano-BioMOFs

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Received 2 May 2016; Revised 29 July 2016; Accepted 7 August 2016

Academic Editor: Zhi Li Xiao

Three new nano-bioMOFs (NBMOFs) (copper serinate, copper prolinate, and copper threoninate) have been hydrothermally synthesized and characterized by the scanning electron microscopy (SEM). Molecular masses of these nanomaterials have been obtained by mass spectrometric studies. Successful *in vitro* drug adsorption of rosuvastatin drug has been carried out in these three nanosized materials. The amount of rosuvastatin adsorbed in these materials and its slow release after intervals have been monitored by the high performance liquid chromatography (HPLC). TGA and PXRD spectra of all these materials in pure form and after rosuvastatin adsorption have also been recorded to elaborate the phenomenon of *in vitro* drug adsorption in these materials.

1. Introduction

Metal organic frameworks (MOFs) have been successfully investigated for their applications in loading and release of several drug molecules. Number of research reports on the use of MOFs as drug delivery materials has been increased during the last three years [1]. Recently some nanoscale regimes in the MOFs have also been reported [2]. Metal organic frameworks can be scaled down to the nanoregime to form nanoscale metal organic frameworks (NMOFs) by using a variety of different techniques that have been developed for inorganic and organic polymeric nanoparticles [3]. Although a large number of the bulk MOF materials have been synthesized and characterized up till now, with the passage of time the number of research reports on the nano-MOFs is also increasing day by day [4].

Due to their ability to control drug release with their large surface areas, high porosity, and presence of functional groups to interact with loaded moieties NMOFs possess a great potential for drugs delivery. This emerging class of NMOFs is now considered as promising candidates for the drug adsorption and its controlled release as well [5].

Although MOFs with high surface areas and structure tunability possess a great potential for the drugs adsorption and its controlled release after some time. But *in vivo* drugs adsorption studies of these MOFs may have compatibility problems inside the body due to their larger sizes [6]. NMOFs have some of the key properties as small size, high drug loading, surface properties, drug release kinetics, improved pharmacokinetics, and biocompatibility [7]. Also NMOFs if incorporated inside the body will reach the targeted organ with high compatibility due to smaller size and will successfully deliver the drug there. So in the recent years NMOFs are being used as drugs delivery vehicles more successfully as compared to MOFs [8].

Rieter et al. have reported the synthesis of nanorods of $Gd(BDC)1.5(H_2O)_2$. These were prepared by $GdCl_3$ and bis(methylammonium)benzene-1,4-dicarboxylate and have been successfully used for the drugs delivery [9]. Rieter et al. have reported a nano-MOF, known as NCP-1, from the Tb^{3+} ions and *c*,*c*,*t*-(diamminedichlorodisuccinato)Pt(IV), a cisplatin prodrug. This relatively potent prodrug has proved a highly potent anticancer drug having a great potential against the cancerous cells. Nano-MIL-101(Fe) is another nano-MOF recently reported by the Rieter group [10]. The amino group if present in MOFs possess a great potential for the successful delivery of drugs so the amino-functionalized nano-MIL-101 was synthesized. It was constructed by incorporating 2-aminoterephthalic acid in the material. The authors have reported the successful adsorption of cisplatin prodrug and

also its controlled release in this amino-functionalized nano-MOF material [11].

While synthesizing the NMOFs one important point is the use of suitable linker molecules and the other is the use of such nontoxic metals without any hazardous side effects to be used for *in vivo* drug adsorption studies [12]. Amino group containing ligands possess a great potential to incorporate with the drugs so amine functionalization of the NMOFs will result in a structure to have great potential for successful drugs adsorption [13]. For *in vivo* drug adsorption studies, the metals used should be nontoxic in construction of MOFs. The metals that are already present in body tissues in certain amounts such as copper (68 μM), manganese (180 μM), nickel (2 μM), and zinc (180 μM) [14] can be easily used in synthesizing nontoxic materials for successful drug delivery applications [15, 16].

This research article basically comprises hydrothermal synthesis of three nano-bioMOFs named "copper serinate," copper prolinate, and copper threoninate. These three nanomaterials have been hydrothermally synthesized from amino acids (serine, proline, and threonine) along with an essential metal (copper).

Scanning electron microscopy of all the three materials has been used to get images of these nanosized materials. Mass spectrometric studies of all these materials have been conducted to know the molecular masses of these nanomaterials. All these materials have been evaluated for their drug adsorption property for rosuvastatin drug. Percentage amount of adsorbed rosuvastatin in all these materials has been estimated through high performance liquid chromatography. TGA and PXRD of all these materials before and after drugs adsorption have also been carried out.

2. Experimental

2.1. Hydrothermal Synthesis of "Copper Serinate". The initial reactions between the serine and copper chloride in the presence of water resulted in the synthesis of a new material named as "copper serinate." For the synthesis of this compound serine linker (0.15 g, 0.2 mmol) and copper chloride, $CuCl_2{\cdot}2H_2O$ (0.35 g, 0.2 mmol), were dissolved in 10 mL water taken in a beaker. This solution was well stirred for half an hour. 10 pH of solution was obtained with the help of sodium carbonate solution. This solution was transferred to a 23 mL Teflon lined autoclave. The autoclave was placed in oven at 150°C for one day. After one day blue colored colloidal solution was obtained from it. This solution was centrifuged and then the blue colored solid particles were separated after sonication and then dried at room temperature. After that the dried powder like material was saved for further characterizations.

Elemental analysis of copper serinate $[Cu(C_3H_6NO_3)_2H_2O]$, Theoretical; Cu = 21.93%, C = 12.43%, H = 4.83%, O = 38.68%, Experimental; Cu = 21.90%, C = 12.39%, H = 4.80%, O = 38.63%.

IR spectra of copper serinate, (4000–400 cm^{-1}), 3599.4 (br) cm^{-1}, 3270.5 (s) cm^{-1}, 3230.7 (m) cm^{-1}, 2910.3 (br) cm^{-1}, 1345.5 (m) cm^{-1}, 1215.6 (m) cm^{-1}, 1180.9 (m) cm^{-1}, 890.9 (m) cm^{-1}, 510.5 (s) cm^{-1}.

2.2. Preparation of Drug Soaked Sample of Copper Serinate. In a typical method 0.1 molar solution of the drug (rosuvastatin) was prepared and copper serinate was soaked in it. The drug solution was removed after twenty four hours and fresh solution was added to the material. The process was repeated for twenty days on regular basis. The rosuvastatin soaked material was removed and saved for characterization. TGA and powder XRD studies were carried out for this drug soaked material.

Some amount of rosuvastatin soaked material was placed in distilled water in a vial and aliquot of water containing released drug was separated from vial after one day. Then same amount of fresh water was added to it and after three days aliquot of water containing released drug was separated from it. The same process was repeated after five, seven, nine, and eleven days of placing the rosuvastatin soaked material in distilled water in vial and all these samples were saved for HPLC studies.

2.3. Hydrothermal Synthesis of "Copper Prolinate". The initial reactions between the proline and copper chloride in the presence of water resulted in the synthesis of new material named "copper prolinate." For the synthesis of this compound proline linker (0.11 g, 0.2 mmol) and copper chloride, $CuCl_2{\cdot}2H_2O$ (0.35 g, 0.2 mmol), were dissolved in 10 mL water taken in a beaker. This solution was well stirred for half an hour. 10 pH of solution was obtained with the help of sodium carbonate solution. This solution was transferred to a 23 mL Teflon lined autoclave. The autoclave was placed in oven at 150°C for one day. After one day blue colored colloidal solution was obtained from it. This solution was centrifuged for some time and then after sonication the blue colored solid material was separated, dried at room temperature, and saved for further characterization.

Drug (rosuvastatin) soaked samples of copper prolinate have been prepared in the same way as have been described above for copper serinate.

Elemental analysis of copper prolinate $[Cu(C_5H_8NO_2)_2H_2O]$, Theoretical; Cu = 20.51%, C = 38.77%, H = 5.81%, O = 25.84%, Experimental; Cu = 20.50%, C = 38.70%, H = 5.75%, O = 25.80%.

IR spectra of copper prolinate, (4000–400 cm^{-1}), 3680.7 (br) cm^{-1}, 3410.9 (br) cm^{-1}, 3290.5 (s) cm^{-1}, 3260.5 (s) cm^{-1}, 3115.6 (br) cm^{-1}, 1650.8 (m) cm^{-1}, 1390.7 (s) cm^{-1}, 1315.5 (s) cm^{-1}, 1280.4 (br) cm^{-1}, 850.6 (br) cm^{-1}, 515.6 (br) cm^{-1}.

2.4. Hydrothermal Synthesis of Copper Threoninate. The initial reactions between the threonine and copper chloride in the presence of water resulted in the synthesis of new material named as "copper threoninate." For the synthesis of "copper threoninate," threoninate (0.12 g, 0.2 mmol) and copper chloride, $CuCl_2{\cdot}2H_2O$ (0.35 g, 0.2 mmol), were dissolved in 10 mL water taken in a beaker. This solution was well stirred for half an hour. 10 pH of solution was obtained with the help

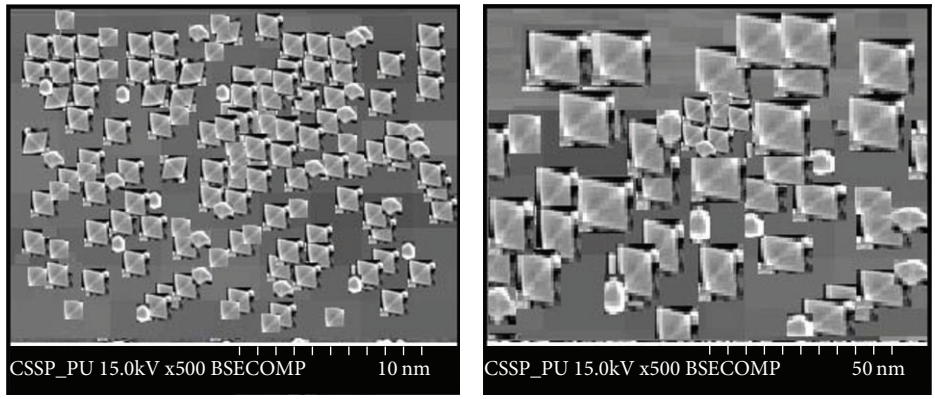

Figure 1: SEM images of "copper serinate" showing the formation of nanosized plate like structures of the material.

of sodium carbonate solution. This solution was transferred to a 23 mL Teflon lined autoclave. The autoclave was placed in oven at 150°C for one day. After one day blue colored colloidal solution was obtained from it. This solution was centrifuged and then blue colored solid material obtained after sonication was dried at room temperature and saved for further characterizations.

Rosuvastatin soaked samples of copper threoninate have been prepared in the same way as have been described above for copper serinate.

Elemental analysis of copper threoninate $[Cu(C_4H_8NO_3)_2H_2O]$, Theoretical; Cu = 20.00%, C = 30.23%, H = 5.66%, O = 35.27%, Experimental; Cu = 19.98%, C = 30.20%, H = 5.60%, O = 35.22%.

IR spectra of copper threoninate; 3660.7 (br) cm^{-1}, 3320.4 (s) cm^{-1}, 3230.5 (m) cm^{-1}, 3160.9 (s) cm^{-1}, 2910.5 (br) cm^{-1}, 1385.7 (m) cm^{-1}, 1310.9 (s) cm^{-1}, 1280.9 (s) cm^{-1}, 1050.9 (br) cm^{-1}, 509.8 (br) cm^{-1}.

3. Results and Discussions

Three new nanosized materials have been hydrothermally synthesized and characterized by scanning electron microscopy (SEM) for determination of morphology. Due to very much small sizes, the assessment of structure of these nanosized crystals of new materials is not possible through the single crystal XRD analysis. Mass spectrometric studies of these three new materials were carried out for the determination of their molecular masses. As these newly synthesized porous materials have been aimed at *in vitro* drug adsorption of rosuvastatin drug these have been synthesized from suitable linkers such as essential amino acids (serine, proline, and threonine) along with a suitable connector like copper metal which is an essential mineral for human body. Therefore obviously these drug carrier materials would have no side effects at all if used for *in vivo* drug adsorption because the human body is already in demand of the constituents from which these materials have been synthesized.

3.1. Scanning Electron Microscopic (SEM) Studies. Scanning electron microscopic images of all three nanomaterials have been obtained from S-3400N which have revealed the formation of the nanosized plate like structures of these materials. So in this manner nano-bioMOF formation has been evaluated by the scanning electron micrographic images of these materials.

For SEM all samples of appropriate sizes are generally mounted rigidly on a specimen holder called a specimen stub. The electron beam, having an energy ranging from 0.2 keV to 40 keV, by one or two condenser lenses is focused to a spot about 0.4 nm to 5 nm in diameter. The beam current absorbed by the specimen was used to create images of the distribution of specimen current. From a high-resolution cathode ray tube the microscopic images were captured, digitised, and saved as digital images.

SEM image of the material "copper serinate" is represented in Figure 1 which indicates the formation of nanosized plate like structures of the material.

SEM image of the material "copper prolinate" indicates the formation of nanoplates of this material as shown in Figure 2. On the other hand Figure 3 shows the morphology of nanosized plate like structure of the material "copper threoninate."

3.2. Mass Spectrometric Studies of Nano-BioMOFs. The molecular masses of "copper serinate," "copper prolinate," and "copper threoninate" have been determined by AB Sciex 3200 Qtrap mass spectrometer. Spectra were obtained by adding together the transient signals recorded from 50 to 200 laser shots using a CAMAC crate based transient recorder and crate controller. The summed spectrum was transferred to a VAX Workstation 3200 for data analysis.

In a typical MS procedure all solid samples were ionized by bombarding them with electrons, some of the sample's molecules to break into charged fragments as a result of this bombardment. According to their mass-to-charge ratio, these ions were then separated, typically by accelerating them and subjecting them to an electric or magnetic field. A mechanism capable of detecting charged particles, such as an electron multiplier, was used to detect the ions. Spectra of the relative abundance of detected ions as a function of the mass-to-charge ratio were displayed as results. Mass spectra of all

Table 1: Measured and calculated molecular masses of copper serinate.

Molecular formula	$[M+H]^+$	Average measured mass (u)	Calculated mass (u)	Difference
$[Cu(C_3H_6NO_3)_2H_2O]$	288.50 289.50 290.50	289.50	289.50	0.00

Table 2: Measured and calculated molecular mass of copper prolinate.

Molecular formula	$[M+H]^+$	Average measured mass (u)	Calculated mass (u)	Difference
$[Cu(C_5H_8NO_2)_2H_2O]$	310.55 309.50 308.57	309.54	309.50	0.04

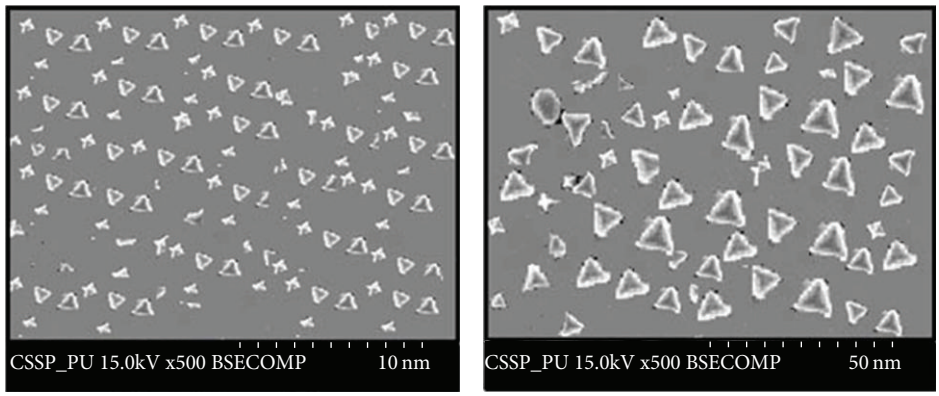

Figure 2: SEM images of the material "copper prolinate," showing the formation of nanoplates of the material.

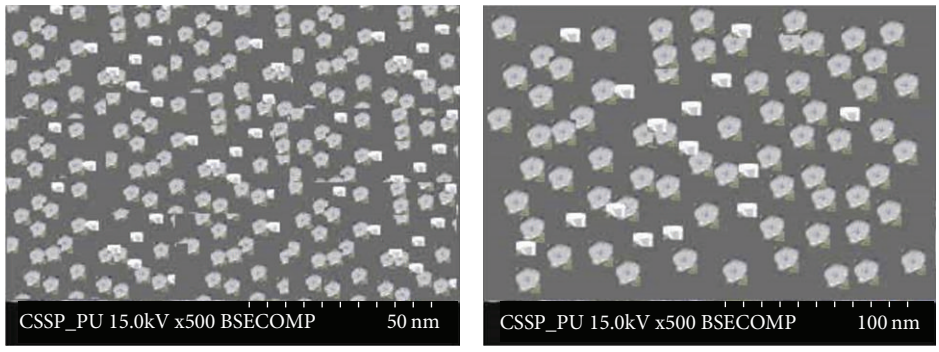

Figure 3: SEM images of the material "copper threoninate" showing the formation of nanoplates of the material.

the three nano-bioMOFs (copper serinate, copper prolinate, and copper histidinate) are given as Figures 4, 5, and 6, respectively, whereas the theoretical and experimental values of molecular masses of copper serinate, copper prolinate, and copper threoninate have been given in Tables 1, 2, and 3, respectively.

3.3. Drug Adsorption in Nano-BioMOFs. All the three materials (copper serinate, copper prolinate, and copper threoninate) have been explored for their drug (rosuvastatin) adsorption capacity. The rosuvastatin has been selected for *in vitro* drugs adsorption studies in all these materials. Because rosuvastatin has applications in treatment of cholesterol and blood sugar levels in human body, the successful incorporation of this drug for *in vitro* studies will lead to its usage for *in vivo* studies as well.

3.4. Thermogravimetric Studies of Nano-BioMOFs

3.4.1. Thermogravimetric Studies of Copper Serinate. Thermogravimetric analyses of the as-synthesized and rosuvastatin adsorbed copper serinate, copper prolinate, and copper

Table 3: Measured and calculated molecular masses of copper threoninate.

Molecular formula	$[M+H]^+$	Average measured mass (u)	Calculated mass (u)	Difference
$[Cu(C_4H_8NO_3)_2H_2O]$	318.60 317.50 316.50	317.53	317.50	0.03

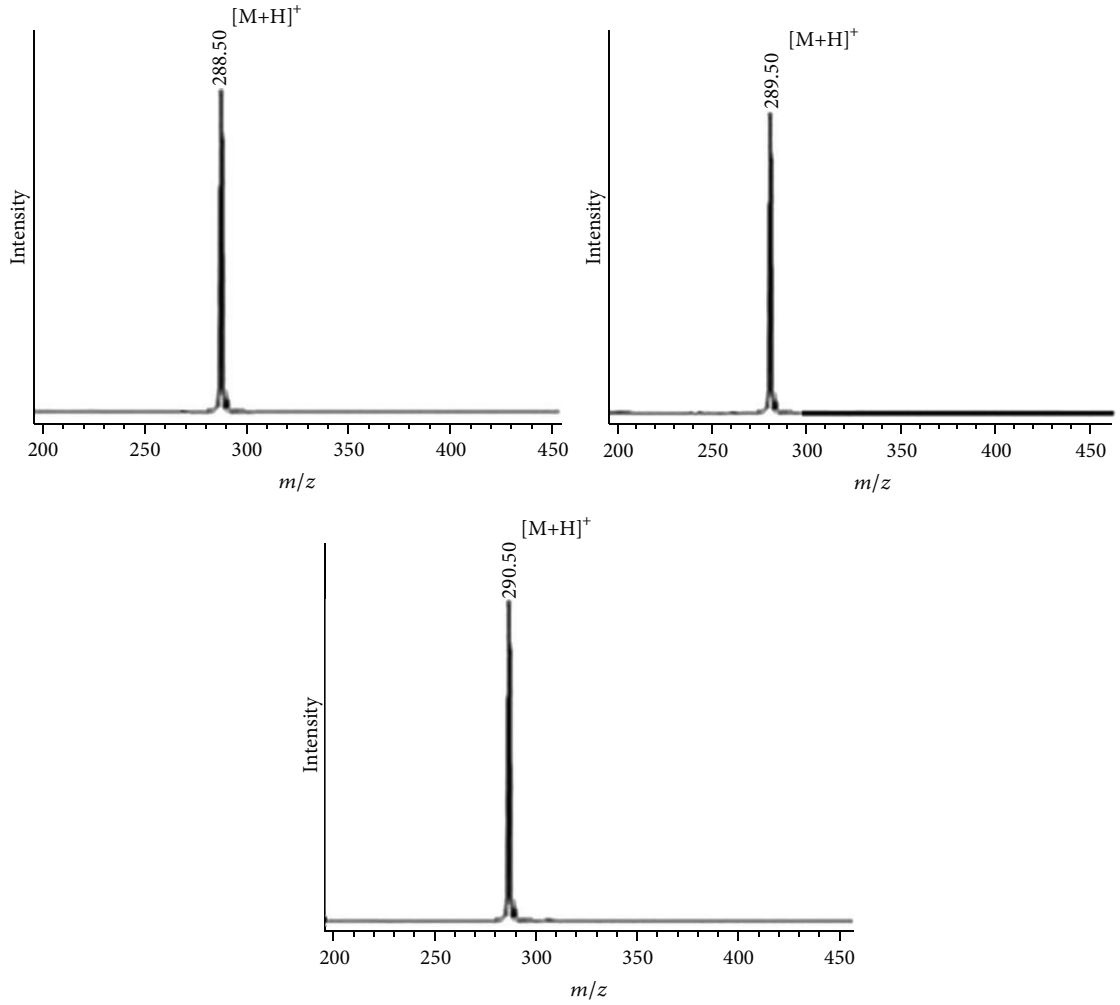

Figure 4: Mass spectra of copper serinate.

threoninate were carried out on a SDT Q600 by heating the compounds from 0°C to 600°C at a heating rate of 10°C per minute.

Before rosuvastatin adsorption the plot of copper serinate in Figure 7 shows first weight loss of 10% at 120°C which is due to the loss of coordinated water molecule. The framework shows stability up to 250°C with no weight loss. At 250°C the decomposition of framework along with ligands starts which continues till 350°C with a 60% weight loss. The framework decomposition continues till 600°C ultimately with the formation of metal oxides as final product.

After rosuvastatin adsorption the plot of "copper serinate" shows a first weight loss of 7% at 45°C, which is due to the loss of drug molecules. After that the framework remains intact for some time and then at 155°C the framework shows a second step of weight loss due to the loss of coordinated water molecule. After that the framework remains intact till 270°C and after 270°C the framework starts to decompose and this decomposition continues up to 320°C with a weight loss of 55%. Then up to 590°C the remaining rosuvastatin contents decompose along with the whole framework.

3.4.2. Thermogravimetric Studies of Copper Prolinate. The plot of "copper prolinate" before rosuvastatin adsorption as given in Figure 8 shows first weight loss of 11% at 125°C due to the loss of coordinated water molecule. The framework remains intact up to 270°C with no weight loss. The decomposition of framework starts at 270°C which continues

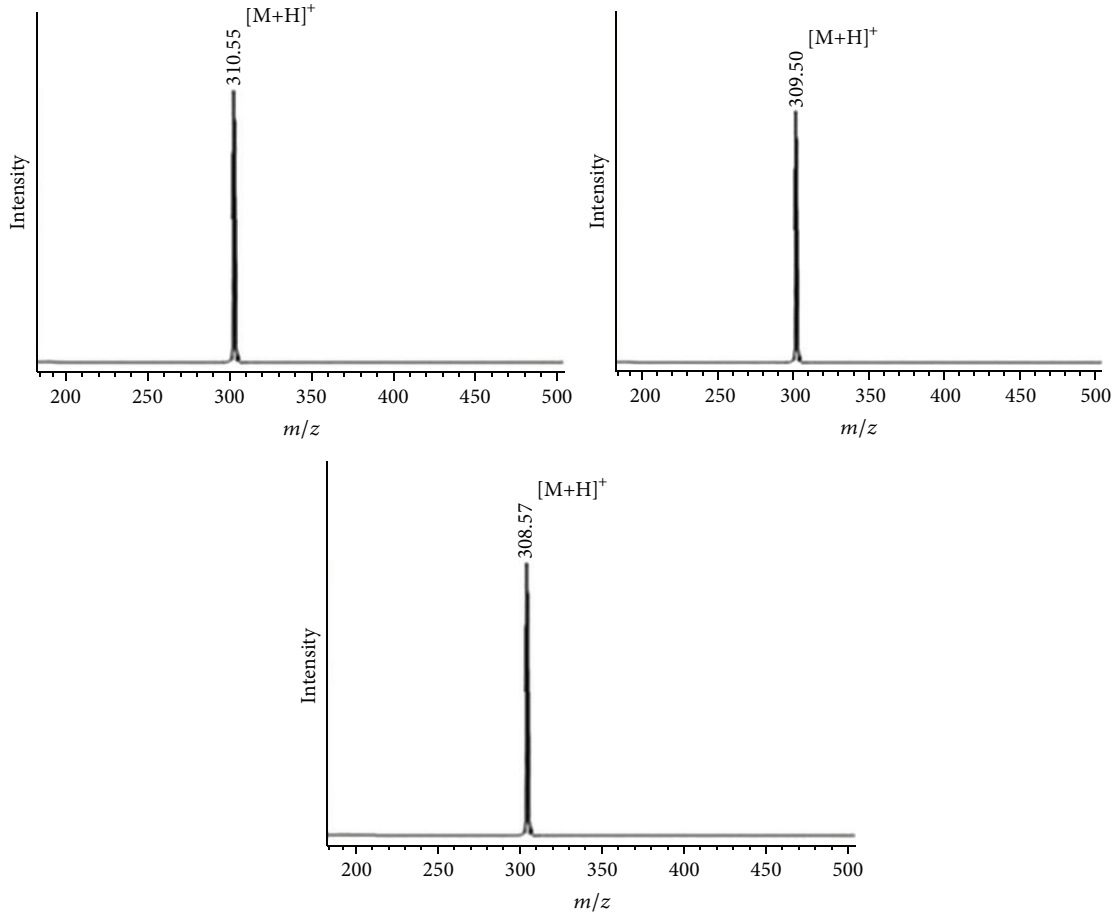

Figure 5: Mass spectra of copper prolinate.

till 370°C with a 62% weight loss. Then up to 600°C the whole framework decomposes ultimately with the formation of metal oxides as final product.

After rosuvastatin adsorption the plot of "copper prolinate" at 48°C shows a first weight loss of 8% due to the loss of rosuvastatin molecules. Then the framework shows stability up to 150°C; after that a second step of weight loss at 150°C indicates the loss of coordinated water molecule. After that up to 300°C the framework remains intact and after 300°C the framework starts to decompose and this decomposition continues up to 320°C with a weight loss of 61%. Up to 600°C the whole framework decomposes along with the remaining rosuvastatin contents.

3.4.3. Thermogravimetric Studies of Copper Threoninate. The plot of "copper threoninate" before rosuvastatin adsorption (Figure 9) shows first weight loss of 9% at 140°C which is due to the loss of coordinated water molecule. After 300°C decomposition of framework starts and gradual decrease in weight due to framework decomposition can be observed until at 600°C the whole framework decomposes with an overall 62% loss of weight.

After rosuvastatin adsorption the plot of "copper threoninate" shows a first weight loss of 8% at 68°C due to the loss of rosuvastatin molecules. Then at 170°C a weight loss of 16% indicates the loss of coordinated water molecule. After 300°C the framework starts to decompose and this decomposition continues up to 340°C with a weight loss of 61%. The framework continues to decompose slowly and gradually and ultimately up to 600°C the whole framework decomposes along with the remaining rosuvastatin contents.

3.5. HPLC Studies for the Estimation of Drug (Rosuvastatin) in Nano-BioMOFs. For the sake of estimation of rosuvastatin contents in the as-synthesized material high performance liquid chromatography (HPLC) was performed on a Waters 2695 separation module. C-18 Luna 5 μ 100 Å (2) Phenomenex was used at ambient temperature.

All the details about the HPLC parameters are given (supporting information in Supplementary Material available online at http://dx.doi.org/10.1155/2016/7803480). It has been determined from HPLC measurements that rosuvastatin drug was adsorbed up to 0.25 g/g material of copper serinate. The maximum time of release of adsorbed amount of rosuvastatin from copper serinate was three days after adsorption as has been estimated from the HPLC studies.

The rosuvastatin was adsorbed up to 0.15 g/g material of copper prolinate. This adsorbed amount of

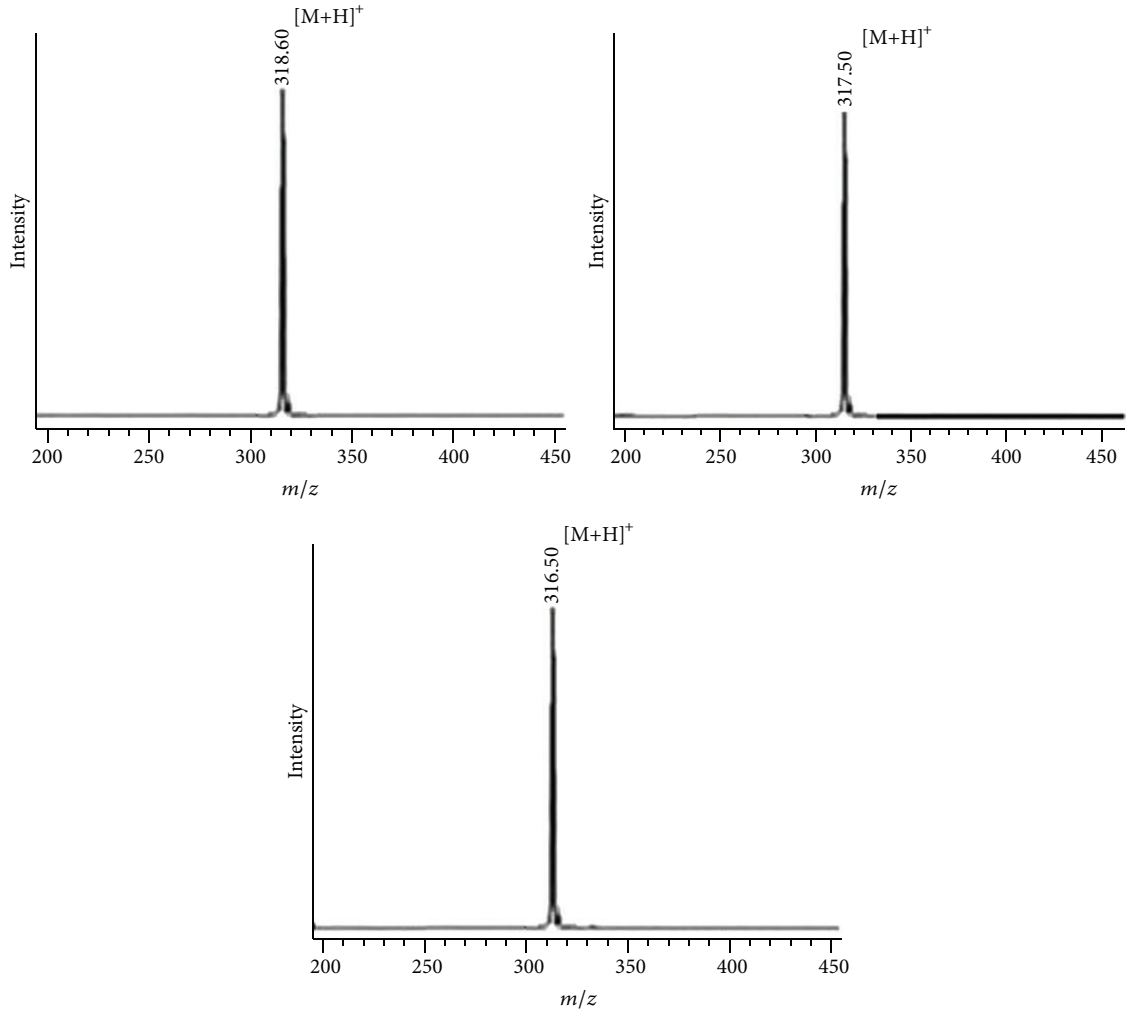

Figure 6: Mass spectra of copper threoninate.

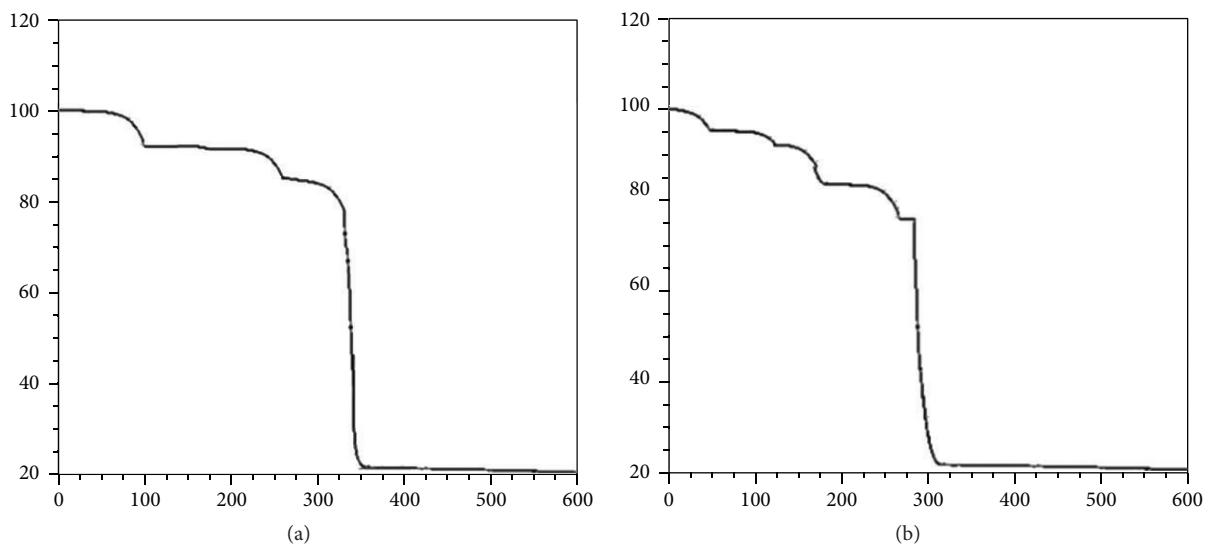

Figure 7: TGA plot of copper serinate, (a) pure, (b) after rosuvastatin adsorption.

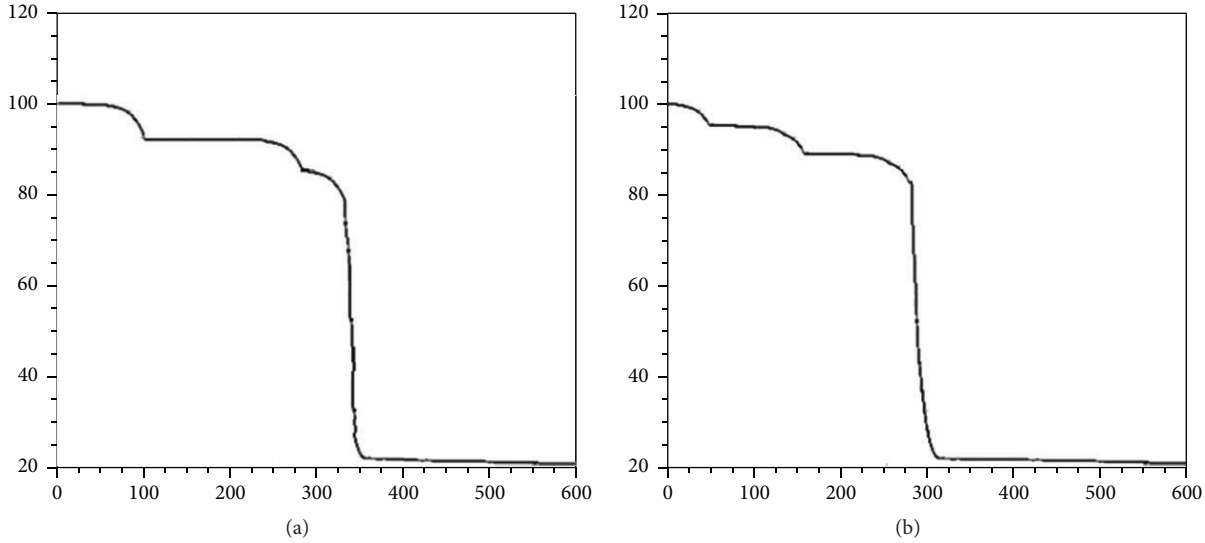

Figure 8: TGA plot of copper prolinate, (a) pure, (b) after rosuvastatin adsorption.

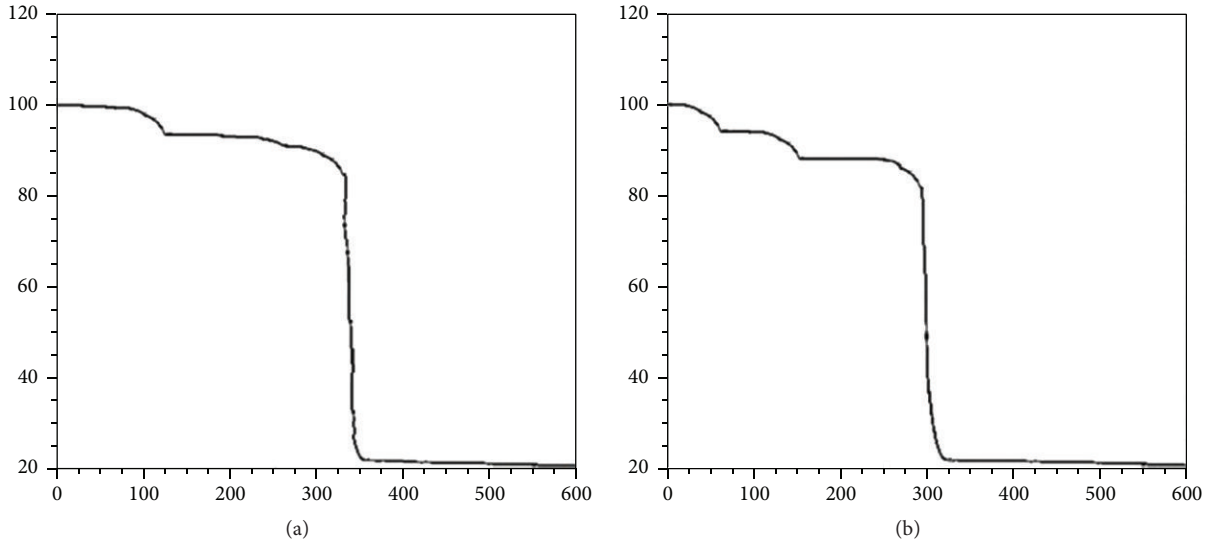

Figure 9: TGA plot of copper threoninate, (a) pure, (b) after rosuvastatin adsorption.

the rosuvastatin was released from the material within five days of adsorption as has been estimated from the HPLC studies.

From HPLC measurements it has been estimated that rosuvastatin was adsorbed up to 0.25 g/g material of copper threoninate. This adsorbed amount of the rosuvastatin was released from the material within five days of adsorption as has been estimated from the HPLC studies.

3.6. Powder XRD Studies of Nano-BioMOFs. Powder XRD patterns of "copper serinate," "copper prolinate," and "copper threoninate" (Figures 10, 11, and 12, resp.) before and after rosuvastatin adsorption have been obtained which have revealed the crystalline integrity of this material. PXRD studies have shown that all the three nano-bioMOFs retain their crystallinity even after soaking them in water for several days. Powder XRD patterns of pure and rosuvastatin adsorbed samples of three nano-bioMOFs are given in Figures 10, 11, and 12.

4. Conclusions

In conclusion the present work is directed towards the hydrothermal synthesis of nanosized bioMOFs which have been successfully utilized for the *in vitro* adsorption of rosuvastatin drug. This work can open new gateway for the more potential use of nanoscale bioMOFs for drug adsorption as compared to large sized bioMOFs that were previously used for drug delivery. Moreover successful *in vitro* drug adsorption experiments on these nanosized materials will lead to their use for *in vivo* drug adsorption as well as for the welfare of humans in medical grounds.

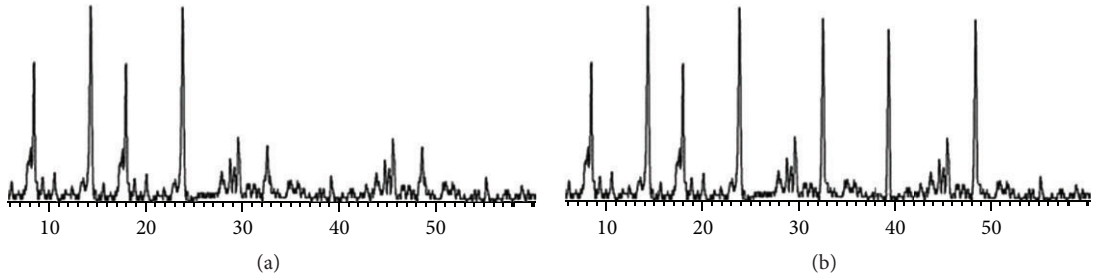

Figure 10: PXRD peaks of copper serinate, (a) pure, (b) after rosuvastatin adsorption.

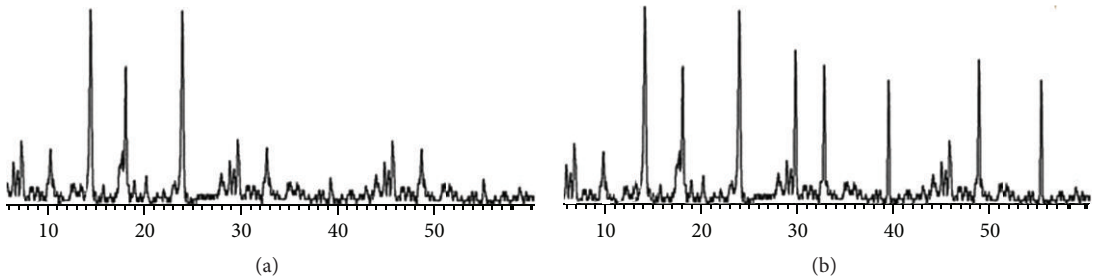

Figure 11: PXRD peaks of copper prolinate, (a) pure, (b) after rosuvastatin adsorption.

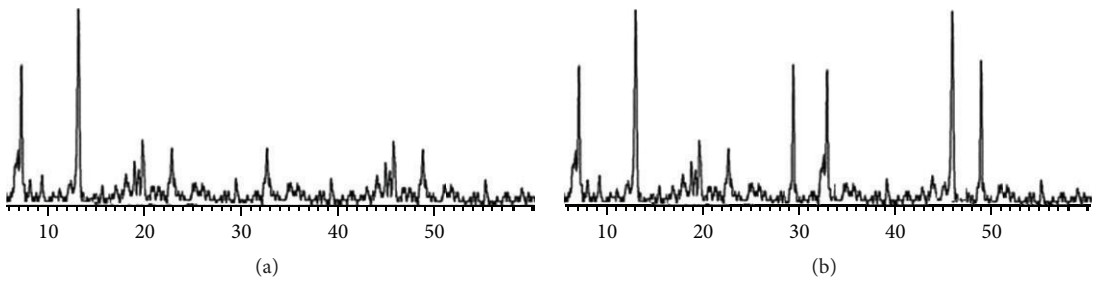

Figure 12: PXRD of copper threoninate, (a) pure (b) after rosuvastatin adsorption.

Competing Interests

The authors declare that they have no competing interests.

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