Asian Journal of Chemistry; Vol. 28, No. 9 (2016), 1949-1954

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.19836

Novel Ionic Liquid Modified Mesomorphorous Materials for Preconcentration of Polysaccharides

YU RI LEE, YU JIN LEE, WANWAN MA, XIAOQIN WANG and KYUNG HO ROW*

Department of Chemistry and Chemical Engineering Inha University, 253 Yonghyun-Dong, Nam-gu, Incheon 402-701, Republic of Korea

*Corresponding author: Fax: +82 32 8720959; Tel: +82 32 8607470; E-mail: rowkho@inha.ac.kr

Received: 12 January 2016; *Accepted*: 11 March 2016; *Published online*: 1 June 2016; AJC-17922

Number 41 silica materials (MCM-41) as mesoporous mobil catalytic materials are attractive for applications to the adsorption and isolation of natural products. In this paper, a new type of MCM-41 material was synthesized by surface modification with an ionic liquid. The new materials were characterized used Fourier-transform infrared spectroscopy and thermogravimetric analysis. High performance size-exclusion chromatography with modified MCM-41 as the stationary phase was used to separate alginate and fucoidan to evaluate the adsorption performance on polysaccharides. The amino-MCM-41 material showed preferable adsorption potency to the polysaccharides. Under the optimal adsorption conditions, namely pH 7.0 and a time 0.5 h and 1 h for alginate and fucoidan, respectively, 68.50 mg g^{-1} alginate and 43.07 mg g^{-1} fucoidan were extracted.

Keywords: Polysaccharide, Ionic liquid, Mesoporous mobil catalytic materials of number, Modification, Alginic acid, Fucoidan.

INTRODUCTION

Polysaccharides are distributed widely in animals, plants and microorganisms and exhibit antitumor [1], anticancer [2], antiviral [3], anticoagulant [4] and immunological activities [5]. Accordingly, polysaccharides from edible and medicinal plants have attracted considerable attention for novel potential antioxidants [6-8]. Brown algaeare a rich source of water-soluble polysaccharides, such as fucoidans and alginic acid.

Fucoidan and alginic acids are the main polysaccharides from brown algae. Fucoidans have antineoplastic, anticoagulant and anticomplementary activities, as well as antiviral activity against the human immunodeficiency, herpes and hepatitis viruses. The structure of alginate varies according to the monomer position on the chain and is composed of mannuronic and guluronic acid with β-(1,4)-linkages, forming either heteropolymeric segments or homopolymeric [9]. Alginic acids have been used successfully in industry and medicine as the basis of tablets and capsules and asenterosorbents for the removal toxins and radio nuclides. To evaluate and predict the bioactivity of polysaccharides, their purification and separation processes are important as the foundations for further study [10].

In the 1990s, researchers from Mobil corporation used a liquid crystal templating approach to synthesize a large family of mesoporous silicates and aluminosilicates, which are known as mesoporous mobil crystalline materials series molecular sieves. Since the discovery of the mesoporous mobil crystalline materials of number 41 series family, the synthesis and applications of mesoporous molecular sieves have attracted considerable interest [11,12]. Mesoporous mobil catalytic materials of number 41 silica materials possess a regular array of hexagonal, uniform, unidimensional mesopores, varying in size from approximately 16 to 100 Å. Owing to its very high surface area and narrow size pore distribution, mesoporous mobil catalytic materials of number 41 silica materials appears in principle to be a good support material. Therefore, many studies examined various aspects of ordered mesoporous materials, such as their surface modification [13], synthesis [14,15], applications as adsorbents [16,17] and catalysis [18,19]. The surface mesoporous mobil catalytic material of number 41 contains no specific functional groups, except for hydroxyl groups. Therefore the adsorption, selectivity and affinity of polysaccharides on mesoporous mobil catalytic materials of number 41 silica materials cannot be controlled. Mesoporous mobil catalytic materials of number 41 silica materials was modified by ionic liquid (IL) to enhance its selectivity by research group [20]. The hydrophobicity, high viscosity, ionic structure, ionic conductivity, low volatility and biocompatibility of ionic liquids make them attractive for electrode modification [21]. The enhanced π-π interactions between the sorbent and target compounds resulted in increased selectivity was reported by Meng and Anderson [22].

In this study, the surface of mesoporous mobil catalytic materials of number 41 silica materials was modified with different functional groups using amino ionic liquids to

increase its surface area and high selectivity for the target compounds. The adsorption isotherm of two polysaccharides and four modifications of mesoporous mobil catalytic materials of number 41 silica materials were compared and the interactions between the modified mesoporous mobil catalytic materials of number 41 silica materials and target compounds were examined.

EXPERIMENTAL

Fucoidan and alginic acid sodium standards were obtained from Sigma Aldrich (St. Louis, MO, USA). Commercial mesoporous mobil catalytic materials of number 41 silica materials (3.0 nm pore diameter, surface area ≥ 800 m^2/g) was purchased from Hailongtech development co. ltd (Binzhou, China). Ethanol, nitric acid and toluene were acquired from Duksan Pure chemical Co. Ltd., (Ansan, Korea). Imidazole (99 %), (3-chloropropyl)trimethoxysilane (≥ 97 %), (3-aminopropyl)-trimethoxysilane (97 %), 3-bromopropylamine hydrobromide (98 %) and triethylamine were supplied by Aldrich (Milwaukee, USA). All other reagents used in the experiment were of high performance liquid chromatography (HPLC) or extra pure grade. Double distilled water was filtered using a vacuum pump (Division of Millipore, Waters, USA) and filter (HA-0.45, Division of Millipore, Waters, USA). All samples were filtered through a filter (Minisart RC 15, 0.45 μm, Goettingen, Germany) before being injected into the HPLC system.

Chromatography conditions: The HPLC system consisted of an YL9112 isocratic pump (Young linco., Anyang, Korea), RI detector (RI750F, Young lininstrument co., Anyang, Korea) and integrated data system (Clarity chromatography software, version 2.3, DateApex, EU). HPLC was performed using a Waters ultrahydrogel™ WATO 11530 size exclusion column (300 × 7.8 mm i.d.) and a Waters ultrahydrogel™ WATO 11565 guard column (40 × 6 mm i.d.) from Waters (Milford, MA, USA). Injection valves with 20.0 μL sample loops were used. The mobile phase was water. The flow-rate and injection volume were set to 0.6 mL/min and 10.0 μL, respectively. Fourier transform infrared (FT-IR, Vertex 80V, Bruker, Billerica, MA, USA) spectroscopy was performed in the range, 4000-400 cm^{-1}, at a scan rate of 20 scans min^{-1}. A KBr pellet was used for analysis. The carbon, hydrogen and nitrogen contents were determined by elemental analysis performed on an elemental analyzer EA1112 (Thermo, Italy). Thermogravimetric analysis (TGA, Scinco thermal gravimeter S-1000) was performed at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere.

Preparation of standard solution: To obtain the standard curves, 2.0, 1.5, 1.0, 0.75 and 0.5 mg mL^{-1} of each the two target compounds were dissolved in water. Subsequently, 10.0 μL of each of the five standard solutions was injected into the HPLC using a size exclusion column.

Synthesis of amino ionic liquid- modified mesoporous mobil catalytic materials of number 41 silica materials: The amino ionic liquid modified mesoporous mobil catalytic materials of number 41 silica materials was synthesized using the method reported elsewhere [20]. A pretreatment was performed to enhance the presence of hydroxyl groups on the mesoporous mobil catalytic materials of number 41 silica materials surface and eliminate any metal oxide and nitrogenous impurities. Mesoporous mobil catalytic materials of number 41 silica materials was activated by stirring with nitric acid/water (50: 50, v/v) for 24 h. The activated mesoporous mobil catalytic materials of number 41 silica materials was filtered and washed thoroughly with distilled water and ethanol and then dried at 120 °C for 12 h.

3-Chloropropyltrimethoxysilane (1 mL) or (3-amino-propyl)trimethoxysilane (0.7 mL) with 2 g mesoporous mobil catalytic materials of number 41 silica materials was stirred and heated under reflux in 50 mL dry toluene. After a 24 h reaction, the powders were washed with ethanol. Chloropropyl mesoporous mobil catalytic materials of number 41 silica material and amino mesoporous mobil catalytic materials of number 41 silica materials were dried under vacuum at 80 °C. Imidazole 0.5 g (with triethylamine catalyst 0.5 g) was then used to modify the chloropropyl mesoporous mobil catalytic materials of number 41 silica materials under reflux in a 50 mL dry toluene. Imidazole-based mesoporous mobil catalytic materials of number 41 silica materials was obtained after heating under reflux for 10 h. The resulting material was washed with ethanol and dried. Subsequently, 2 g imidazole-based mesoporous mobil catalytic materials of number 41 silica materials and 2 g 3-bromopropylamine hydrobromide were stirred in 50 mL of ethanol and heated under reflux for 24 h. After the reaction, the amino ionic liquid-modified mesoporous mobil catalytic materials of number 41 silica materials was obtained.

Preparation of adsorption isotherm: The static method was performed on the amino-mesoporous mobil catalytic materials of number 41 silica materials, imidazole-based mesoporous mobil catalytic materials of number 41 silica materials and amino ionic liquid-modified mesoporous mobil catalytic materials of number 41 silica materials particles. 2 mg of amino-mesoporous mobil catalytic materials of number 41 silica materials, imidazole-based mesoporous mobil catalytic materials of number 41 silica materials and amino ionic liquid-modified mesoporous mobil catalytic materials of number 41 silica materials was placed, separately, into microtubes and mixed with 1 mL of water and the standard solutions (0.50, 0.75, 1.00, 1.50, 2.00 mg mL^{-1}) at room temperature for 0.5 h with constant stirring. The adsorption solution was centrifuged and the supernatant solvent was collected and filtered. The experimental adsorption isotherms were fitted to the following three models: linear, Freundlich adsorption isotherm and Langmuir-Freundlich models. This process was accomplished using the solver function in OriginPro 8.0 software (Origin Lab Corporation, MA, USA) by varying the fitting parameters until the squared correlation coefficient (r^2) reached unity.

RESULTS AND DISCUSSION

To obtain the standard curves, alginate and fucoidan solutions with accurate concentrations were produced by dilution (0.50, 0.75, 1.00, 1.50 and 2.00 mg mL^{-1}) with water. The resulting linear regression equations of the two compounds were $Y = 136.03x - 8.3505$ ($r^2 = 0.9928$) for alginate and $Y = 83.54x - 6.815$ ($r^2 = 0.9974$) for fucoidan. The precision was determined by repeating the analysis six times and the method recovery ranged from 97.4 to 100.7 %. Assays of the repeatability calculated as the relative standard deviations (RSDs)

were performed by injecting the extraction sample 5 times in a 5-day period. The RSDs were lower than 5.12 % showing acceptable precision and accuracy (Table-1). These results show that the proposed method is stable with a wide range of potential applications. The amount (Q) of alginate and fucoidan adsorbed on mesoporous mobil catalytic materials of number 41 silica materials, amino-mesoporous mobil catalytic materials of number 41 silica materials, imidazole-based mesoporous mobil catalytic materials of number 41 silica materials and amino ionic liquid-modified mesoporous mobil catalytic materials of number 41 silica materials were determined using the following equation:

$$Q = \frac{(C_0 - C)V}{m} \quad (1)$$

where Q (mg g^{-1}) is the amount absorbed, C_0 (mg mL^{-1}) is the initiator concentration, C (mg mL^{-1}) is the free concentration, V (mL) is the volume of the sample solvent and m (mg) is the dry mass of the sorbent. Q was calculated using eqn. 1. The experimental parameters were compared by non-linear regression analysis using the equilibrium isotherms.

The IR spectra of mesoporous mobil catalytic materials of number 41 silica materials and its modified mesoporous mobil catalytic materials of number 41 silica materials shows that the hydroxyl group absorbs between 3600 to 3200 cm^{-1} (Fig. 1). The signal of the hydroxyl group in a new material is lower than that of mesoporous mobil catalytic materials of number 41 silica materials [20,23,24]. The presence of the N–H bending vibration around 3400 cm^{-1} and the C=N stretching in the range of 1515 cm^{-1} confirmed the incorporation of imidazole groups. The absorbance of the H–N–H stretching vibration is normally observed at approximately 1627 and 1390 cm^{-1} [25]. Therefore, the ionic liquid groups successfully replaced the –OH groups on the mesoporous mobil catalytic materials of number 41 silica materials surface.

Fig. 2 presents the TGA profiles of the three modified mesoporous mobil catalytic materials of number 41 silica materials and parent mesoporous mobil catalytic materials of number 41 silica materials samples. All samples showed an initial weight loss at approximately 150 °C, which was assigned to the loss of physically adsorbed water interacting with the hydrophilic surface. With increasing temperature, the weight loss of mesoporous mobil catalytic materials of number 41 silica materials and imidazole-based mesoporous mobil catalytic materials of number 41 silica materials remained constant, indicating no appreciable condensation of silanol groups on the surface. The weight loss curves of amino-meso-

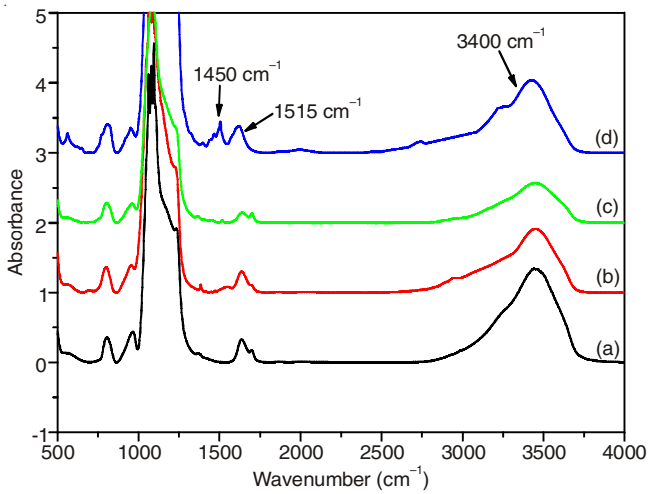

Fig. 1. FTIR of mesoporous mobil catalytic materials of number 41 series (a) mesoporous mobil catalytic materials of number 41 silica materials, (b) amino-mesoporous mobil catalytic materials of number 41 silica materials, (c) imidazole-based mesoporous mobil catalytic materials of number 41silica materials, (d) amino ionic liquid-modified mesoporous mobil catalytic materials of number 41silica materials

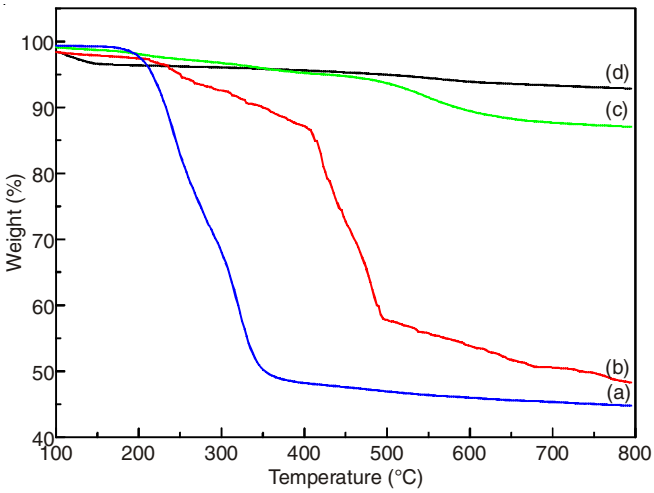

Fig. 2. TGA weight loss curves of the mesoporous mobil catalytic materials of number 41 silica materialsseries (a) amino ionic liquid-modified mesoporous mobil catalytic materials of number 41silica materials, (b) amino-mesoporous mobil catalytic materials of number 41 silica materials, (c) imidazole-based mesoporous mobil catalytic materials of number 41 silica materials, (d) mesoporous mobil catalytic materials of number 41 silica materials

porous mobil catalytic materials of number 41 silica materials and amino ionic liquid-modified mesoporous mobil catalytic materials of number 41 silica materials showed three regions

TABLE-1
INTRA-DAY AND INTER-DAY PRECISIONS, ACCURACIES AND RECOVERIES OF ALGINATE AND FUCOIDAN WITH THREE DIFFERENT CONCENTRATIONS

Analyte	Concentration (μg mL^{-1})	Intra-day		Inter-day		Method recovery (%)
		Measured concentration (μg mL^{-1})	Precision RSD (%)	Measured concentration (μg mL^{-1})	Precision RSD (%)	
Alginate	1	1.01 (±0.21)	4.61 (±1.25)	0.99 (±2.20)	3.89 (±2.54)	99.4
	50	50.12 (±3.48)	3.54 (±4.08)	49.98 (±5.00)	4.54 (±2.82)	100.7
	100	99.08 (±1.54)	3.69 (±2.58)	100.25 (±2.88)	4.11 (±5.12)	98.1
Fucoidan	1	0.98 (±0.18)	3.71 (±4.01)	1.00 (±1.05)	4.60 (±3.07)	99.7
	50	49.14 (±0.24)	3.39 (±0.28)	51.07 (±3.85)	3.82 (±2.24)	97.4
	100	100.78 (±2.85)	4.32 (±1.22)	99.98 (±2.87)	4.75 (±1.32)	98.2

(Fig. 2). First, the weight loss up to 150 °C refers to the loss physically adsorbed water. Second, the weight loss between 200 and 300 °C indicated the appreciable condensation of a ligand with any residual silanol on the surface and with silanols on the neighboring ligands. Third, the weight losses at 320 and 700 °C were assigned to the decomposition of the organic ligand bonded chemically to the surface. These results indicate the different stability of the organic moieties in the samples, which could be due to a distinct location or binding to the silica surface [24,26].

The highest percentage of carbon and nitrogen on amino-mesoporous mobil catalytic materials of number 41 silica materials, imidazole-based mesoporous mobil catalytic materials of number 41 silica materials and amino ionic liquid-modified mesoporous mobil catalytic materials of number 41 silica materials showed that the ionic liquid group was immobilized on mesoporous mobil catalytic materials of number 41 silica materials (Table-2). As a result, immobilization of the amino group was successful.

TABLE-2
ELEMENTAL ANALYSIS OF MODIFIED MESOPOROUS MOBIL CATALYTIC MATERIALS OF NUMBER 41SILICA MATERIALS

Sorbent	C (%)	H (%)	N (%)
MCM-41	2.15	1.06	–
NH_2-MCM-41	5.95	2.43	2.10
Im-MCM-41	6.57	1.37	2.03
NH_2-IL-MCM-41	11.61	2.89	4.17

MCM-41 (Mesoporous mobil catalytic materials of number 41 silica materials), NH_2-MCM-41 (amino-mesoporous mobil catalytic materials of number 41 silica materials), Im-MCM-41 (imidazole-based mesoporous mobil catalytic materials of number 41 silica materials), NH_2-IL-MCM-41 (amino ionic liquid-modified mesoporous mobil catalytic materials of number 41 silica materials)

Optimization of adsorption conditions

Effect of pH: The pH of an aqueous medium is an important factor that can affect the uptake of an adsorbate. The chemical characteristics of both the adsorbent and adsorbate vary according to pH. The pH of the solution affects the degree of ionization and the speciation of various pollutants, which leads to a change in the reaction kinetics and equilibrium characteristics of the adsorption process. The effects of the initial pH on the adsorption of alginates and fucoidan by mesoporous mobil catalytic materials of number 41 silica materials were studied. In the alkaline range, the pH was varied using aqueous NaOH, whereas in the acidic range, the pH was varied using HCl [27]. Fig. 3 shows the experimental results for the uptake of alginates and fucoidan on amino-mesoporous mobil catalytic materials of number 41 silica materials at a pH of 1, 3, 7, 9 and 11. This shows that the adsorption capacity of amino-mesoporous mobil catalytic materials of number 41 silica materials decreases significantly at low pH (2–3) and high pH (10–11). The maximum amounts of alginate and fucoidan at pH 7 was 68.50 mg g^{-1} and 43.70 mg g^{-1}, respectively. NH_2-MCM-41 is a material with amphoteric characteristics. Therefore, their surfaces might be positively or negatively charged depending on the pH, which has a direct influence on the electrostatic interactions [28-30]. In addition, a higher or lower pH will not favour adsorption of the basic dye on amino-

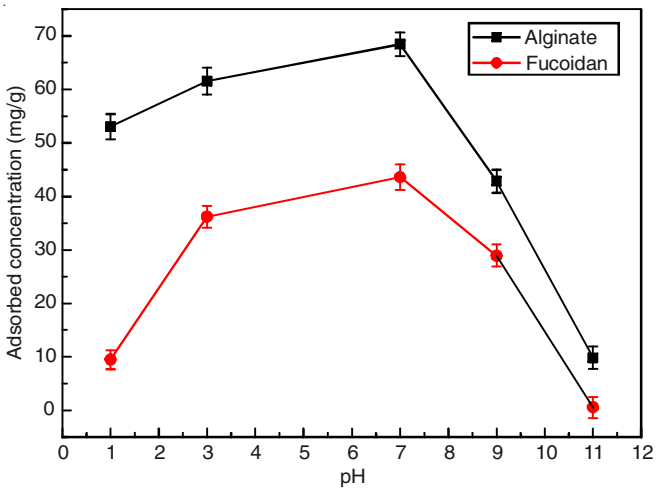

Fig. 3. Effects of pH on the adsorption efficiency (amino-mesoporous mobilcatalytic materials of number silica materials, concentration: 1.5 mg g^{-1}, time of alginic acid: 30 min, time of fucoidan: 60 min, Sorbents added amount: 20 mg, solvent: water)

mesoporous mobil catalytic materials of number 41 silica materials. Some other effects of the pH on the dyes and amino-mesoporous mobil catalytic materials of number 41 silica materials structure should be also considered. For example, the structure of amino-mesoporous mobil catalytic materials of number 41 silica materials might not be stable in acid solutions and the dyes can decompose in acid solutions [31].

Effect of time: Fig. 4 shows the effect of time on amino-mesoporous mobil catalytic materials of number 41 silica materials at a concentration of 1.5 mg g^{-1}, 20 mg of the added sorbents and water as the solvent. In addition, the time was varied from 30 to 150 min to optimize the time. A sharp decrease in the amount adsorbed with time was observed. The optimal time for alginate and fucoidan was found to be 30 min and 60 min, respectively. The experimental results showed that amount of alginate and fucoidan adsorbed was 68.50 mg g^{-1} and 40.43 mg g^{-1}, respectively. This suggests that with alginate, adsorption is complete at 30 min. After 30 min, a desorption process occurs. With fucoidan, adsorption is complete at 60 min. After 60 min, the desorption process occurs (Table-3). This is relevant to the bonding of a large number of hydroxyl groups on the adsorbent surface to water through hydrogen bonding. After a certain time, there were difficulties in forming hydrogen bonds between the hydroxyl groups remaining on the adsorbent and water molecules and the adsorption of water reached equilibrium [32].

Adsorption isotherms: The equilibrium adsorption isotherm is important in the design of adsorption systems. The effects of different functional groups in mesoporous mobil catalytic materials of number 41 silica materials series were evaluated. The experimental data of alginate and fucoidan was fitted to the following three adsorption isotherm models:

$$Q = a\frac{bC_E}{1 + bC_E} \quad (2)$$

$$Q = aC_E^b \quad (3)$$

$$Q = \frac{abC_E^{1-c}}{1 + bC_E^{1-c}} \quad (4)$$

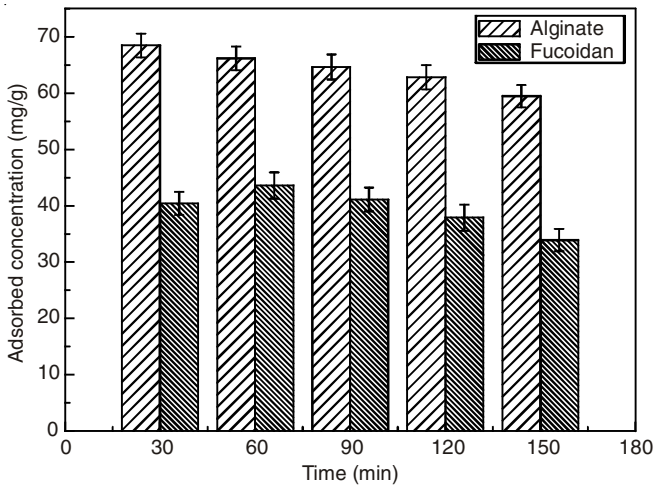

Fig. 4. Effect of time on the adsorption efficiency (amino-mesoporous mobil catalytic materials of number 41 silica materials, concentration: 1.5 mg g^{-1}, Sorbents added amount: 20 mg, solvent: water)

TABLE-3
ADSORBED AMOUNT OF STANDARD SOLVENT WITH DIFFERENT SORBENTS

Conc. (mg g^{-1})	Sorbents	Adsorbed amount (mg g^{-1})	
		Alginate	Fucoidan
2.00	MCM-41	38.315	6.802
	NH_2-MCM-41	53.606	8.669
	Im-MCM-41	39.260	20.436
	NH_2-IL-MCM-41	3.345	1.888
1.50	MCM-41	2.869	0.548
	NH_2-MCM-41	68.50	40.431
	Im-MCM-41	21.00	22.70
	NH_2-IL-MCM-41	0.560	0.326
1.00	MCM-41	3.223	0.350
	NH_2-MCM-41	39.660	18.826
	Im-MCM-41	22.263	23.172
	NH_2-IL-MCM-41	0.838	0.428
0.75	MCM-41	23.881	1.760
	NH_2-MCM-41	34.431	33.421
	Im-MCM-41	19.654	22.564
	NH_2-IL-MCM-41	0.295	1.855
0.50	MCM-41	14.028	20.921
	NH_2-MCM-41	21.931	20.921
	Im-MCM-41	14.403	20.921
	NH_2-IL-MCM-41	3.876	2.223

Sorbents added amount: 20 mg, solvent: water, time: 30 min, MCM-41 (mesoporous mobil catalytic materials of number 41silica materials), NH_2-MCM-41 (amino-mesoporous mobil catalytic materials of number 41 silica materials), Im-MCM-41 (imidazole-based mesoporous mobil catalytic materials of number 41 silica materials), NH_2-IL-MCM-41 (amino ionic liquid-modified mesoporous mobil catalytic materials of number 41silica materials)

where a, b and c are parameters and C_E (mg mL^{-1}) is the concentration of alginate and fucoidan in the standard solution samples. The adsorption isotherm models used were the Langmuir (eqn. 2), Freundlich (eqn. 3) and Langmuir-Freundlich (eqn. 4). Table-4 listed the adsorption parameters using the three adsorption isotherm models. The regression coefficient (r^2) of the competitive Langmuir-Freundlich isotherm for alginate and fucoidan was 0.9887 and 0.9908, respectively. Therefore, the Langmuir-Freundlich isotherm was used to better compare the competitive adsorption. The Langmuir adsorption isotherm is generally applied to a homogeneous adsorption system. Freundlich presented the earliest known experimental equation for the adsorption of a material onto animal charcoal. This is an empirical equation used to describe heterogeneous systems and is not restricted to the formation of a monolayer [17].

Conclusion

This study compared the ability of mesoporous mobil catalytic materials of number 41 silica materials *e.g.*, amino-mesoporous mobil catalytic materials of number 41 silica materials, imidazole-based mesoporous mobil catalytic materials of number 41 silica materials and amino ionic liquid-modified mesoporous mobil catalytic materials of number 41 silica materials to adsorb two target compounds, alginate and fucoidan. Among the four mesoporous mobil catalytic materials of number 41 silica materials series, amino-mesoporous mobil catalytic materials of number 41 silica materials showed the best adsorption of the target compounds. Under the optimized conditions of the solvent of water and pH 7.0, 68.50 mg g^{-1} and 43.70 mg g^{-1} of alginate and fucoidan were obtained in 30 and 60 min, respectively. Among the adsorption isotherm models, the Langmuir-Freundlich isotherm was found to be the optimal isotherm for this study. The regression coefficient (r^2) of the competitive Langmuir-Freundlich isotherm for alginate and fucoidan was 0.9887 and 0.9908.The acceptable validation parameters and simple procedure indicates that the HPSEC method is a suitable method for separating the soluble polysaccharides in brown seaweed based on the molecular weight. The use of ordered mesoporous materials for adsorption is a growing but still challenging field with a high demand for new and improved materials.

ACKNOWLEDGEMENTS

This work was supported by the National Research Foundation of Korea (NRF) grant funded by Korea Government (MSIP) (No.NRF-2014R1A2A2A05002046).

TABLE-4
PARAMETERS FOR THE ADSORPTION ISOTHERM OF THE TWO TARGET COMPOUNDS BY AMINO-MESOPOROUS MOBIL CATALYTIC MATERIALS OF NUMBER 41 SILICA MATERIALS

Target compounds	Parameters	a	b	c	r^2
Alginate	Langmuir	95.503	0.637	-	0.9850
	Freundlich	36.234	0.585	-	0.9716
	Langmuir-Freundlich	70.483	1.167	-0.361	0.9887
Fucoidan	Langmuir	62.589	0.965	-	0.9654
	Freundlich	29.970	0.487	-	0.9286
	Langmuir-Freundlich	44.158	2.712	-0.907	0.9908

REFERENCES

1. S.P. Wasser, *Appl. Microbiol. Biotechnol.*, **60**, 258 (2002).
2. Y.O. Kim, H.W. Park, J.H. Kim, J.Y. Lee, S.H. Moon and C.S. Shin, *Life Sci.*, **79**, 72 (2006).
3. M.Witvrouw and E. De Clercq, *Gen. Pharmacol.*, **29**, 497 (1997).
4. B. Mulloy, P.A.S. Mourao and E. Gray, *J. Biotechnol.*, **77**, 123 (2000).
5. Z. Zhao, J. Li, X. Wu, H. Dai, X. Gao, M. Liu and P. Tu, *Food Res. Int.*, **39**, 917 (2006).
6. W. Xu, F. Zhang, Y.B. Luo, L. Ma, X. Kou and K. Huang, *Carbohydr. Res.*, **344**, 217 (2009).
7. T. Takada, T. Katagiri, M. Ifuku, N. Morimura, M. Kobayashi, K. Hasegawa, A. Ogamo and R. Kamijo, *J. Biol. Chem.*, **278**, 43229 (2003).
8. L.S. Costa, G.P. Fidelis, S.L. Cordeiro, R.M. Oliveira, D.A. Sabry, R.B.G. Cβmara, L.T.D.B. Nobre, M.S.S.P. Costa, J. Almeida-Lima, E.H.C. Farias, E.L. Leite and H.A.O. Rocha, *Biomed. Pharmacother.*, **64**, 21 (2010).
9. T.N. Zvyagintseva, N.M. Shevchenko, I.B. Popivnich, V.V. Isakov, A.S. Scobun, E.V. Sundukova and L.A. Elyakova, *Carbohydr. Res.*, **322**, 32 (1999).
10. H. Zhang and K.H. Row, *J. Carbohydr. Chem.*, **33**, 225 (2014).
11. M. Vallet-Regi, A. Ra'mila, R.P. del Real and J. Pérez-Pariente, *Chem. Mater.*, **13**, 308 (2001).
12. M. Kruk, M. Jaroniec and A. Sayari, *J. Phys. Chem. B*, **101**, 583 (1997).
13. M.J. Jia, A. Seifert and W.R. Thiel, *Chem. Mater.*, **15**, 2174 (2003).
14. E.P. Ng, J.Y. Goh, T.C. Ling and R.R. Mukti, *Nanoscale Res. Lett.*, **8**, 120 (2013).
15. J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins and J.L. Schlenker, *J. Am. Chem. Soc.*, **114**, 10834 (1992).
16. X.S. Zhao, G.Q. Lu and X. Hu, *Micropor. Mesopor. Mater.*, **41**, 37 (2000).
17. M. Ghiaci, A. Abbaspur, R. Kia and F. Seyedeyn-Azad, *Sep. Purif. Technol.*, **40**, 217 (2004).
18. A. Corma, *Chem. Rev.*, **97**, 2373 (1997).
19. J.A. Wang, X. Bokhimi, O. Novaro, T. López, F. Tzompantzi, R. Gómez, J. Navarrete, M.E. Llanos and E. López-Salinas, *J. Mol. Catal. Chem.*, **137**, 239 (1999).
20. M.L. Tian, W.T. Bi and K.H. Row, *J. Chem. Technol. Biotechnol.*, **87**, 165 (2012).
21. M. Opallo and A. Lesniewski, *J. Electroanal. Chem.*, **656**, 2 (2011).
22. Y. Meng and J.L. Anderson, *J. Chromatogr. A*, **1217**, 6143 (2010).
23. E.K. Yoda, J.N. Kondo, F. Wakabayashi and K. Domen, *Appl. Catal. A*, **194–195**, 275 (2000).
24. P. Pal, S.K. Rastogi, C.M. Gibson, D.E. Aston, A.L. Branen and T.E. Bitterwolf, *ACS Appl. Mater. Interfaces*, **3**, 279 (2011).
25. F.P. Shang, J.R. Sun, S.J. Wu, Y. Yang, Q. Kan and J. Guan, *Micropor. Mesopor. Mater.*, **134**, 44 (2010).
26. P. Iliade, I. Miletto, S. Coluccia and G. Berlier, *Res. Chem. Intermed.*, **38**, 785 (2012).
27. P.A. Mangrulkar, S.P. Kamble, J. Meshram and S.S. Rayalu, *J. Hazard. Mater.*, **160**, 414 (2008).
28. R. Saad, K. Belkacemi and S.F. Hamoudi, *J. Colloid Interf. Sci.*, **311**, 375 (2007).
29. J.J.M. Órfão, A.I.M. Silva, J.C.V. Pereira, S.A. Barata, I.M. Fonseca, P.C.C. Faria and M.F.R. Pereira, *J. Colloid Interf. Sci.*, **296**, 480 (2006).
30. Q.D. Qin, J. Ma and K. Liu, *J. Hazard. Mater.*, **162**, 133 (2009).
31. L.C. Juang, C.C. Wang and C.K. Lee, *Chemosphere*, **64**, 1920 (2006).
32. B.K. Tang, W.T. Bi and K.H. Row, *Appl. Biochem. Biotechnol.*, **169**, 1056 (2013).