Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Investigation of five metal organic frameworks as sorbent in syringe filters-SPE method for determination of metronidazole and cephalexin in water samples

Soleyman Moinfar[a*], Ali Khodayari[b], Helan Zyad Sami[a], Maher Khalid Ali[c], Nobahar Nezar Abdi[a]

[a]Scientific research center, University of Zakho, Zakho, Iraq

[b]Department of Chemistry, Faculty of Science, University of Mohaghegh Ardabili, 56199-11367, Ardabil, Iran

[c]Department of Chemistry, Faculty of Science, University of Zakho, Zakho, Iraq

[*]Corresponding author:

Tel: +9647515236229

E-Mail: soleiman_moinfar@yahoo.com, soleiman.moeinfar@uoz.edu.krd

Chemicals and Reagents

Pure drugs including metronidazole (98%) was supplied from (sigma-aldrich, San Diego, USA), cephalexin (98%) and vancomycin (98%) were supplied from (Danna Pharma Co, Tabriz, Iran), chromium (III) nitrate nonahydrate ($Cr(NO_3)_3.9H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3.9H_2O$), aluminum sulfate octadecahydrate ($Al_2(SO_4)_3.18H_2O$), aluminum chloride hexahydrate ($AlCl_3.6H_2O$), zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$), Nitric acid (HNO_3), Sodium hydroxide (NaOH), terephthalic acid (C_6H_4-1,4-$(CO_2H)_2$), fumaric acid and all organic solvents were from Merck (Germany). The synthetic grade 2-aminoterephthalic acid ($H_2NC_6H_3$-1,4-$(CO_2H)_2$) was purchase from Sigma Aldrich company (USA). All chemicals were of synthesis grade, and used without any further purification. Separate standard solutions containing 500 mg/L of each drugs were prepared in mixture of ultra-pure water, 90%, and CAN, 10%, and kept at 4ºC. Fresh working solutions were prepared by appropriate dilution of standard solutions prior to analysis.

2.5. Synthesis of the AlFu

Aluminum fumarate metal-organic framework (AlFu) was synthesized using reflux-assisted co-precipitation approach. To this end, 4.6 mmol of fumaric acid was inserted into 20 ml of deionized water. Then, 0.7 mL of 50% sodium hydroxide solution was added drop-wise while the solution was getting mixed on a magnetic stirrer at 700 rpm. Once the fumaric acid was completely dissolved in water, it was transferred to a 100-ml volumetric flask. In another container, 3.3 mmol of $Al_2(SO_4)_3.18H_2O$ was dissolved in 20 mL of deionized water and added to sodium fumarate solution drop-wise under vigorous mixing. The solution was refluxed at 90 ºC for 2 hours and cooled down at room temperature post reaction completion. The resulting white color powder was washed once with ethanol and three times with deionized water in order to remove unreacted raw materials as well as reaction byproducts. Then, it was vacuum dried at 80 ºC for 24 hours.[1] Finally, the dried powder was heated in a furnace at 320 ºC for 24 hours to remove water molecules and unreacted terephthalic acids that may have capsulated inside the pores of AlFu.

2.7. Synthesis of the IRMOF-3

2.5 mmol of 2-aminoterephthalic acid and 7.5 mmol of zinc nitrate hexahydrate together with 60 mL of (dimethyl formamide) DMF were placed in a Teflon container and stirred at 600 rpm for 5 minutes. Then, the Teflon container was transferred to a steel capsule, followed by heating at 100 ºC for 24 hours in an electric oven. Next, the capsule was cooled down room temperature and the upper aqueous layer was drained out. The obtained crystalline product was rinsed by DMF three times, 10 mL each time. Then, it was placed in DMF and stirred at 150 rpm on a shaker for 24 hours. Afterwards, it was transferred to a flask containing chloroform and left for 3 days to remove the excess DMF. Finally, the solid product was separated from chloroform, dried out at room temperature, and heated at 100 ºC in an oven for 24 hours.[2]

2.8. Synthesis of the NH_2-MIL-101(Al)

In order to prepare NH_2-MIL-101(Al), 4.2 mmol of $AlCl_3.6H_2O$, 6.2 mmol of 2-aminoterephthalic acid and 60 mL of DMF were mixed together according to a previously reported method.[3] Each reactant was first dissolved in the solvent, DMF, by stirring on a magnetic stirrer. The obtained

solution was then heated at 130 ºC for 72 hours in a Teflon lined autoclave to complete the chemical reaction. Next, the autoclave was left at room temperature to cool down, and the obtained yellow powder was separated by the aim of centrifuge. Afterwards, the collected powder was washed out with acetone three times, and activated in boiling methanol overnight. The solution was then cooled down, and the solid phase was separated by centrifuge. The collected porous material was then dried out at room temperature and heated at 100 ºC in an oven for 12 hours.

2.9. Synthesis of the NH_2-MIL-101(Cr)

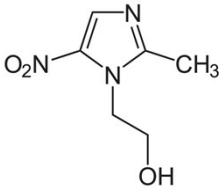
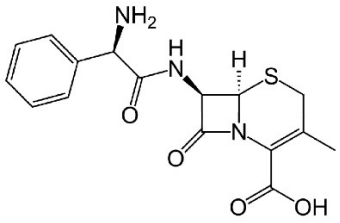
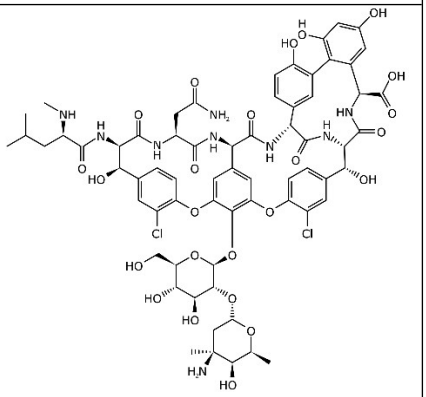
The synthesis of NH_2-MIL-101(Cr) was performed according to a published study.[4] In summary, 8 mmol of terephthalic acid and 8 mmol of Cr $(NO_3).9H_2O$ were put in a Teflon reactor, and 60 mL of 0.33 M NaOH was added drop-wise. The whole mixture was stirred at 700 rpm for 60 minutes to obtain a homogenous mixture. Then, the reactor was heated at 160 ºC for 16 hours, cooled down at ambient condition, and the solid product was separated by centrifuge at 7000 rpm for 5 minutes. The resulting powder was rinsed by deionized water several times, and then washed successively with DMF and methanol to remove residual organic species. The treated powder was finally dried at 100 ºC for 24 hours in an oven.

Table S1

Special surface area and porosity properties of MOFs used

MOFs	**BET surface area ($m^2 g^{-1}$)**	**Total pore volume ($cm^3 g^{-1}$)**	**Mean diameter (nm)**
IRMOF3	741.37	0.65	3.75
NH_2-MIL-101(Al)	536.58	0.35	2.42
NH_2-MIL-101(Cr)	793.06	0.58	2.69
AlFu	519.14	0.26	1.84
MIL-53(Al)	1032.60	0.44	1.71

Table S2

Antibiotics	**Metronidazole**	**Cephalexin**	**Vancomycin**
Formula	$C_6H_9N_3O_3$	$C_{16}H_{17}N_3O_4S$	$C_{66}H_{75}Cl_2N_9O_{24}$
Molar mass ($g\ mol^{-1}$)	171.16	347.39	1449.27
Solubility in water at 20℃ ($g\ L^{-1}$)	10	0.297	50
Structure	 [5]	 [6]	 [7]

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