ISBN: 978-978-68-0485-9 DOI: https://doi.org/10.55455/acsnigeria.1.2.38-43

Synthesis of Aluminium Metal-Organic Frameworks for the Removal of Emerging Pollutants from Aqueous Solution: Kinetics and Thermodynamics

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ABSTRACT

Serious environmental and human health problems caused by emerging pollutants have attracted worldwide concern and recently, metal–organic frameworks (MOFs) with high porosity have drawn global attention for their effects on the adsorption efficiency for the removal of emerging pollutants from the environment. In this study, aluminium based metal-organic frameworks (MIL-53) were synthesized by the hydrothermal method. The synthesized MOFs were characterized using Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET) surface analysis and used as suitable adsorbent to remove Amoxicillin, Bromophenol blue, and Methyl red from simulated aqueous solutions. The influences of different parameters such as adsorbent dosage, contact time, initial ion concentration, and temperature were investigated and the results indicated that the adsorption process followed pseudo-second order. Five well-known models including Langmuir, Freudlich, Temkin, Reddlich-Peterson, and Jossen's 3P were employed to correlate the experimental data obtained from the batch adsorption experiments and the thermodynamic studies show that the adsorption of the pollutants on the synthesized MOFs is spontaneous and feasible. Consequently, MOFs-53 with a high adsorption performance has potential applications for the removal of emerging contaminants from wastewater. In line with the Millennium developments and Sustainable Goals MDGs/SDGs Vision 2030, the findings seek to address a crucial component of environmental protection and public health by unveiling the development of cheap, effective, and sustainable adsorbent materials for tailored scale more efficient water filtration and purification technology.
KEYWORDS: MOFs, Adsorption isotherms, Emerging pollutants, Thermodynamic studies

1. INTRODUCTION

Modern society presently characterized with rapid growth, industrialization, urbanization and several anthropogenic activities in the quest to comfort life has consequently increased the release of several groups of pollutants into water bodies, endangering aquatic ecosystems and public health.[1] These set of pollutants are known as emerging pollutants which includes textile waste, industrial chemicals, pharmaceuticals, personal care items, agricultural chemicals and other generated domestic waste substances which have currently drawn increasing attention because of their potential threat to the physiological anatomy of living organisms even at low concentrations due to their persistence, and bioaccumulativecharacteristics.[2] The inefficiency of conventional water treatment techniques to effectively eliminate these contaminants makes the innovation of sophisticated and more potent remediation technologies necessary such as the (MOFs) adsorbent a considerable option for sustainable development.[3]

Reports in recent years have seen a significant increase of interest in metal-organic frameworks (MOFs), which is conceived as a family of porous crystalline materials made of metal ions or clusters coupled to organic ligands characterized to be employed for use in several environmental remediation applications. They are promising options for the adsorption of different pollutants from aqueous solutions due to their large surface area, adjustable porosity, and chemical adaptability.[4,5]Aluminium-based MOFs are particularly well-suited for industrial water treatment applications because of their cost-effectiveness, non-toxicity, as well as thermal and chemical stability.[6,7]

The synthesis and design of aluminium metal-organic frameworks and their usage in eliminating amoxicillin, bromophenol blue, and methyl red from aqueous solutions are the main topics of this investigation. To gain a better understanding of the mechanisms behind the interaction between MIL53(Al) and the targeted contaminants, special attention is paid to examining the adsorption kinetics and thermodynamic characteristics. This research work is in correlation with the global millennium and sustainable development goals.

2. MATERIALS AND METHODS

2.1. Materials. Terephthalic acid (%), aluminium nitrate nonahydrate, N, N-dimethylformamide (DMF), Bromophenol blue, Methyl red, Methanol, and 2-Propanol were purchased from Sigma Aldrich. Amoxicillin was provided by Eurolink Nigeria Ltd., Jos-Nigeria. All reagents used were of analytical grade.

2.2. Preparation of Al-MOFs. A modified version of a previously reported process[8,9] was used to synthesize Al-based MOFs under hydrothermal conditions. In 70 mL of a solution (30 mL DMF: 20 mL 2-propanol: 20 mL distilled water), precisely 1.21g of teraphthalic acid was added to it. An aluminium nitrate nonahydrate of 1.53 g was then dissolved in the solution of terephthalic acid, DMF, propanol, and distilled water. After 30 minutes of agitating, the mixture was transferred to a Teflon-lined stainless autoclave reactor and heated to 130 °C for four hours. Methanol was used to filter and wash the crystal product for five days. The remnant traces of contaminants from the mixture were evaporated by activating MIL-53(Al) for72 hours at 130 °C.

2.3. Characterization. The synthesized Al-MOFs were characterized using FT-IR, XRD, BET, and SEM.

2.4. Simulation of the Stock Solution of the Contaminants

2.4.1. Preparation of Amoxicillin (AM), Bromophenol Blue (BB), and Methyl Red (MR)Stock Solutions. Amoxicillin, Bromophenol blue, and Methyl red stock solutions of 250 mg/L using distilled water and the required standard concentrations were obtained by serial dilution of the stock solution.

2.5. Batch Adsorption Experimental Methods. Sorption tests were carried out to investigate the adsorption behavior of the Al-based MOFs. A comparative study was performed to estimate and evaluate the adsorption capacity and kinetic model for removing AM, BB, and MR from the water. This method allowed the accurate estimation of the rate at which pollutants were adhered to the surface of the porous materials. During the entire set of experiments, a range of parameters were examined to analyze their effect on the adsorption process. Among the parameters were initial ion concentration (50 to 250 mg/L), adsorbent doses (0.15 to 0.75 g/L), contact time (30 to 150 minutes), and temperature (30 to 70 ^{o}C). Each mixture was then agitated at 3000 rpm for 30 minutes using a centrifuge. The solution mixture was then filtered and the adsorption extent of AM, BB, and MR were determined using UV-Vis spectrophotometer at wavelengths of 272, 590, and530 nm, respectively. The amount and percentage of ion adsorbed were calculated for each experiment using the equations adopted in previous studies reported (Rafatullah et al.,).[10]

3. RESULTS AND DISCUSSION

3.1. Characterization. FT-IR spectra of MIL-53(Al) adsorbent and after adsorbing the pollutants are shown in Figure 1. The substantial reduction in the peak between 600 and 1500 cm^{-1} after adsorption could be as a result of the pollutants adhered to the surface and filling the pores of the MOFs[11].Figure 2 shows the MIL-53's XRD patterns. The steep peak indicates that the MOFs are crystalline while Figure 3 shows that the pore size distribution was 2.1 nm, indicating it is a nanoparticle as determined by BET. Figure 4 as well, shows the SEM image at 100 µm which described the structure of MOFs-53 to be crystalline having high porosity and large surface area.

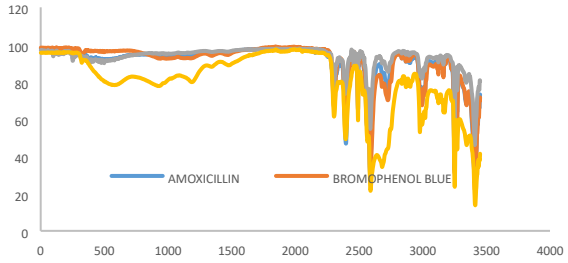

Figure 1. FT-IR Spectra of MIL-53(Al)

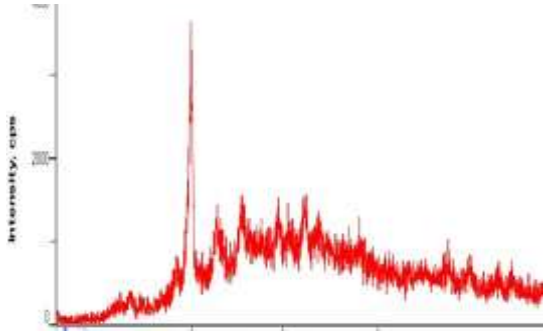

Figure 2. XRD of MIL-53(Al)

ACS Chapter Nigeria Book of Proceedings 10th Annual Symposium

ISBN: 978-978-68-0485-9 DOI: https://doi.org/10.55455/acsnigeria.1.2.38-43

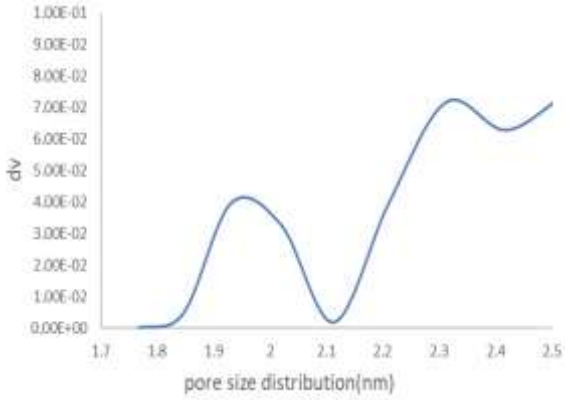

Figure 3. BET of MIL-53(Al)

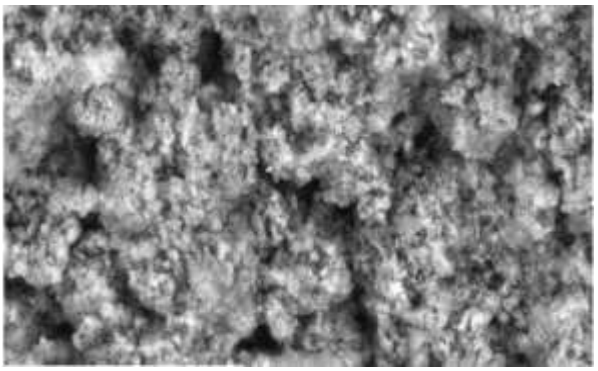

Figure 4. SEM image of MIL-53(Al) at 100 µm

3.2. Batch Adsorption Studies. It was deduced from Table 1, that the removal rate of AM, BB, and MR decreases with an increase in the starting ion concentration. At larger concentrations, the adsorbent active sites become saturated, which results in a decrease in percentage removal. As seen in Table 2, the adsorption capacity further increased as the adsorbent dosage increased from 0.15 to 0.75 g which suggested that more sites became available for holding and engulfing the contaminants in the water. Table 3 also, shows how temperature affects the pollutants' ability to be adsorbed. Consequently, at 30 °C, a rapid adsorption of contaminates by the MOFs was observed which suggests that these contaminants are most effectively removed at a relatively low temperature and the highest and optimal removal of the contaminants at the ideal contact time of 150 minutes, with a small deviation in the case of methyl red, is depicted in Table 4 together with the observed removal in percentage at various timing ranges.

3.3. Adsorption Isotherms. Adsorption isotherms are used to explain how the adsorbent and adsorbate are in equilibrium. The equilibrium adsorption data were evaluated using Freundlich, Langmuir, Jossen's 3P, Reddlich-Peterson, and Temkin isotherm models and the predicted values are presented in Table 5.

Table 1. Effect of Initial Ion Concentration

Conc. (mg/L)	Percentag	
	AM	BB
20	97.967	95.8
40	96.967	81.2
40	95.622	74.4
80	95.300	63.5
100	94.744	57.4

Table 2. Effect of Adsorben

Dosage (g)	Percentag	
	AM	BB
0.15	90.967	76.0
0,30	91.522	79.4
0.45	93.967	80.5
0.60	94.633	84.4
0.75	95.411	85.5

Table 3. Effect of Temperature

Temp. (K)	Percentage Removal		
	AM	BB	MR
303	94.189	85.136	84.078
313	93.633	81.045	77.019
323	93.967	79.227	73.098
333	93.522	73.318	70.745
343	93.189	71.955	68.196

Table 4. Effect of Contact Time

Time (mins)	Percentage Removal		
	AM	BB	MR
30	92.744	95.364	75.450
60	94.189	95.819	73.294
90	92.077	96.045	69.960
120	93.189	96.273	67.607
150	94.522	96.727	65.450

Abuja, Nigeria - May 4-7, 2025

ACS Chapter Nigeria **Book of Proceedings** 15th Annual Symposium

ISBN: 978-978-68-0485-9 DOI: https://doi.org/10.55455/acsnigeria.1.2.38-43

3.4. Adsorption Kinetics. The Pseudo second-order model[12,13]was used to evaluate the mechanisms controlling the process of the contaminant adsorption from the aqueous solution, such as chemical reaction, mass transfer, and diffusion control. Table 6 shows the results of the model's evaluation for the plotted experimental data which depicted a correlation coefficient (R^2) of 1.000, 0.911, and 0.999 for AM, BB, and MR, respectively, hence these results demonstrated excellent fit and linearity. **Table 5. Isotherm Parameters**

Isotherms	Parameters	Values		
		AM	BB	MR
Freundlich	R^2	0.979	0.854	0.989
	n	-29.325	-4.985	10.245
	K_F (L/g)	7.093	0.996	11.400
Langmuir	R^2	0.952	0.855	0.996
	Qmax (mg/g)	19.194	0.413	2.149
	B (L/mg)	0.122	-4.101	-5.267
Temkin	R^2	0.879	0.904	0.990
	K_T (Lg^{-1})	1.260	-5.045	0.002
	b ($Jmol^{-1}$)	9876.940	-19551.270	-2721.816
Reddlich-Peterson	ß	1.061	1.201	1.1000
	A	7.563	2.463	11.473
	R^2	1.000	0.995	1.000

Jossen's 3P	F	-0.222	-0.098	-0.646
	H	0.001	0.404	0.015
	R^2	0.985	0.942	0.992

Table 6. Pseudo-Second-Order Kinetic Parameters

Equation	Parameters	Values		
		AM	BB	MR
Pseudo- second- order	q_e(mg/g) cal.	0.178	0.444	2.348
	K_2	6.450	-0.191	-0.061
	R^2	1.000	0.911	0.999

Table 7. Thermodynamic Parameters

T(K)	ΔG(kJ/mol)			ΔH (J/mol)			ΔS (J/mol.K)			R^2		
	AM	BB	MR	AM	BB	MR	AM	BB	MR	AM	BB	MR
303	- 6.343	-6.949	-5.838	472.131	357.739	194.480	22.495	24.115	19.910	0.953	0.949	0.992
313	-6.568	-7.190	-6.037									
323	-6.793	-7.431	-6.236									
333	-7.018	-7.672	-6.435									
343	-7.243	-7.913	-6.634									

3.5. Thermodynamic Studies. The thermodynamic studies revealed temperature affects the contaminant adsorption processes in two ways; The first one is that an increase in temperature leads to a higher diffusion rate of the adsorbent and secondly, the adsorption capacity at equilibrium is also influenced by temperature which is in agreement with previous reported similar studies.[14] The Gibbs and Van't Hoff plots were used to evaluate the free energy (ΔG) where heats of adsorption (ΔH) and changes in the system entropy (ΔS), determine the viability of the adsorption process, and the

parameters are presented in Table 7.The observations of negative values of ΔG show that the process is feasible and spontaneous. Furthermore, the endothermic nature of the adsorption process was emphasized by the positive values of ΔH AM (472.131 J/mol), BB, (357.739 J/mol), and MR (194.480 J/mol) respectively). The degree of randomness at the MOFs or adsorbate solution interface is improved by the rate of pollutants' adsorption on MIL-53(Al), as indicated by the positive values of ΔS for AM (22.49 J/K), BB (24.115 J/K), and MR (19.91 J/K) respectively.[15]

CONCLUSION

Al-MOFs was synthesized and designed by mixing different solvents and the characterization results revealed the material as crystalline, Porous with good pore sizes and stable to both physical and chemical conditions. The results of its high rate of absorption and removal of Amoxicillin, Bromophenol blue, and Methyl red from the simulated aqueous solution also demonstrated the efficiency of these

MOFs with high adsorbing capacity to remove these three pollutants significantly in water. The optimal conditions that favor Amoxicillin, Bromophenol blue, and Methyl red adsorption and removal from water were as follows: adsorbent dosage (0.75, 0.75, and 0.15 g), contact time (150, 150, and 30 mins), initial ion concentration (20 mg/L), and temperature (30 ° C) respectively. It was observed also, that the process was entirely endothermic, practicable, and spontaneous. Therefore, Al-based (MOFs) can be highly considered and used as an efficient adsorbent for wastewater treatment in real-world applications.

ACKNOWLEDGEMENTS

The authors acknowledge and appreciate Eurolink Nigeria Ltd., Jos, Plateau State for supporting this research with some valuable chemicals.

CONFLICT OF INTERESTS

The authors declare no conflict of interests.

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