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Adsorptive Removal of Chromium (III) From Aqueous Solution Using Funtionalized MIL53: Amine, Sulfonic, and Cyano groups

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Abstract:

Metal-organic frameworks (MOFs) based on 1,4-benzenedicarboxylic acid Were synthesized and modified via post-synthetic modification, incorporating sulfonic, cyano, and amino functional groups. Various techniques, including Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM/EDS), thermogravimetric analysis and differential thermal analysis (TGA-DTA), and Brunauer-Emmett-Teller (BET), used to assess the functional group, structures, surface area, thermal stability, and pore characteristics. The results confirmed successful incorporation of SO₂H, CN, and NH₂ functional groups into the MOFs. The adsorption capacities of the MOFs show that MIL-53+CN adsorbent has the highest adsorption capacity (q_e values) of 59 mg/g, followed by MIL-53+SO₂H (55.75) mg/g, while MIL-53+NH₂ adsorbent has the lowest adsorption capacity of 49 mg/g. Thermodynamic analysis indicated an exothermic adsorption process. Also, Response surface methodology (RSM) with Box-Behnken Design (BBD) was used to optimize adsorption conditions, including concentration (10-100 mg/L), pH (4-10), and dosage (0.01-0.05 g). The model predicted maximum adsorption yields for MIL-53+SO₃H, MIL-53+CN and MIL-53+NH₂, with values of 96, 79 and 92.06 mg/g, respectively, under specific conditions. The results demonstrate the potential of functionalized MOFs, particularly MIL-53+SO₃, for the selective removal of Cr(III) metal ions from aqueous media.

Keywords: MOFs, MIL-53, Amine, Cyano and Sulfonic, Adsorption Study, Thermodynamic Study,

Introduction

Due to the fast development of the global economy and expansion of urbanization over the last few decades, pollution of surface and groundwater with heavy metals and their adverse effects on the health of living organisms, as well as the consequent problems, have received considerable attention (Ghanbarian et al., 2020, Khoso, et al., 2021). The main sources of heavy metals include mining, smelting, battery manufacturing, textile printing and the leather industries (Azimi et al., 2017). Heavy metals, such as chromium (Cr), is difficult to degrade and easily accumulate in the wastewater due to it can easily solubility, high toxicity and bioaccumulation in the food chain and within the ecosystem (Fu et al., 2011). Various adsorbents such as kaolinite, zeolites, montmorillonite clay and activated carbon-nanotube (Ali 2012) have been developed to remove dissolved pollutants such as heavy metals from the solution, but these adsorbents have low adsorption capacity for heavy metals because of the limited voids available. In this regard, designing a promising nano-porous adsorbent such as Metal–Organic Frameworks (MOFs) is considered to be a significant. MOFs have received significant attention in recent years due to their wide range of potential applications and their vast contact surface areas, solvent stabilities, high porosity, well-organized pores, and regular particle size (Li et al., 2012, Xiang et al., 2011). They are usually self-assembled materials, built from transition metal ions and bridging organic ligands, forming periodic network structures (Vahdat et al., 2019). Owing to their porosity, ordered, and well characterized porous structures, adjustable chemical functionality and Host-guest interactions (Kaur et al., 20).

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The MIL-53 series is a typical class of MOFs with the advantages of flexible structure, stable chemical properties and breathing feature stability (L. Xie *et al.*, 2019). Furthermore, the high-valence metal ion center of Fe^{3+} with the most commonly used carboxylate-type ligands can be easily applied to synthesize water-stable MOFs (L. Xie *et al.*, 2019, W. C *et al.*, 2016).

In general, modifying the properties of MOFs by incorporating specific functional groups is an effective strategy to improve the adsorption performance of adsorbents. Besides, the technique of incorporation can be simply achieved by importing functional groups onto organic ligands (Li *et al.*, 2015). Hence, in this research work, the $-\text{NH}_2$, $-\text{SO}_2\text{H}$ and $-\text{CN}$ groups were introduced in MIL-53(Fe) by a one-step solvothermal method. The physical and chemical properties of the functionalized MIL-(53) adsorbents were characterized using Fourier transform infrared spectrum (FTIR), Scanning electron microscope (SEM), X-ray powder diffractometer (XRD), and Brunauer-Emmett-Teller (BET). The adsorption performance of functionalized MIL-53(Fe) for Cr (III) ion adsorption was investigated and the thermodynamic adsorption mechanisms were proposed. Also, the design of the experimental was carried out using Box-Behnken Design (BBD) based on response surface methodology (RSM) to optimize the adsorption reaction conditions for the adsorptive removal of Cr (III) ions were analyzed.

Methodology

Materials and reagents

All chemicals were of analytical grade, purchased from commercial sources and used without further purification. Ligands: Terephthalic acid (TPA) and 1,4-benzenedicarboxylic acid. Functionalizing Agent: Ethylenediamine, Metal Salts: Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), Chromium(III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and Titanium(IV) isopropoxide (TBOT) were obtained from (Sigma Aldrich). Solvents: N,N'-dimethylformamide, Methanol, Ethanol, Hydrofluoric acid, Toluene and Deionized water.

Synthesis of MIL-53

Mil-53(Fe) was synthesized based on the method reported by (Pu *et al.*, 2018), with slight modifications. 1.35 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5 mmol) and 0.83 g of terephthalic acid (5 mmol) were dissolved in 25 mL of N,N'- dimethylformamide. The solution was transferred to a 100 mL Teflon-lined autoclave and heated in the oven at 150 °C for 15 h. The resulting samples were collected by filtration, washed with 150 mL methanol and 150 mL of ethanol successively.

Functionalization of MIL-53

Prior before functionalization, the MIL-53 was activated at 150 °C for 12 hours to get rid of the occluded solvent molecules and also generated coordinatively unsaturated sites needed for the attachment of the introduced functional groups. Thereafter, different functional groups were incorporated into the MIL-53 structure (Luo *et al.*, 2015), as follows:.

Sulphonic acid functionalization

0.1g of the MIL-53 was suspended in 10mL anhydrous toluene. 0.11 g of (1 mmol) aminomethanesulfonic acid in toluene 5 mL was added and the mixture was stirred at room temperature for 24 hours. The resulting solid was filtered and dried at 100 °C for three hours.

Cyano-functionalization

MIL-53 sample of about 0.1g was suspended in 10 mL of anhydrous toluene in a conical flask. 0.132 g of (2 mmol) malononitrile was added to the suspension and the mixture was stirred at room temperature for 24 hours. The resulting solid was filtered and dried at 100 °C for three hours.

Amine- functionalization

0.1g of the synthesized MIL-53 sample was suspended in 10 mL of anhydrous toluene. 1 mL of ethylenediamine was added to the suspension and the mixture was stirred at room temperature for 24 hours. The resulting solid was filtered and dried at 100 °C for three hours. The Sulphonic, cyano and amine functionalization of the MIL-53 were carried out based on the report described (Luo *et al.*, 2015).

Characterization

Powder X-ray diffraction (XRD) patterns of the samples were obtained by a Rigaku D/MaxIIIc, PW1800. Fourier transform infrared (FTIR) spectra were recorded on a SHIMADZU-FTIR (FTIR-8400s) apparatus with KBr method. The morphologies and the microstructure of the synthesized samples were characterized by scanning electron microscopy (SEM) operated on a JEOL-JSM-7600F. The BET surface area measurement was performed with N_2 adsorption-desorption isotherms at liquid nitrogen temperature (77 K) after the samples were dehydrated under vacuum at 383 K for 12 h using a Micromeritics TriStar II 3020. A ContrAA 700 (Analytik Jena, Germany) high resolution continuum source atomic absorption spectrometer (AAS) was used for the determination of Cr (III) ions.

Adsorption Studies for Cr (III) ions Metal

All adsorption experiments were done in batches following a procedure reported by (Guo J *et al.*, 2019). Adsorption of Cr (III) ions unto the functionalized MOFs was investigated using spiked samples containing various metal concentrations (10

– 100 mg/L). 50 mL solution of the spiked samples was agitated with 0.1 g of MOF adsorbents at 150 rpm for 240 min at 298 K while the pH is adjusted to 6. The sample solution was separated from the MOF adsorbents via centrifugation and the residual metal concentration was determined using Atomic

Absorption Spectrophotometric method. The effects of operational parameters such as pH, contact time and adsorbent dosage was optimized using the design expert software. The quantity of metal ion absorbed was estimated using the formula:

$$q = \left(\frac{C_i - C_f}{m} \right) v \quad 1$$

Where q is the adsorption capacity of a (mg/g), C_i and C_f are the initial and final concentrations of the adsorbate respectively, v is the volume of solution used (mL) and m is the mass (g) of the adsorbents.

Thermodynamic Experiments

A thermodynamic study shows the effect of temperature on the adsorption process of functionalized MOFs. Generally, there are two common types: endothermal and exothermal sorption

processes. If the sorption increases with increasing temperature, it means that the sorption is an endothermal process. Whereas the adsorption decreases with increasing temperature, it indicates the exothermic adsorption process. The thermodynamic parameters such as free energy (ΔG_0), enthalpy (ΔH_0) and entropy changes (ΔS_0) for the sorption are calculated using the following equations:

$$\Delta G = -RT \ln K \quad 2$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{T} \quad 3$$

$$\Delta G = \Delta H - T\Delta S \quad 4$$

Where R is the ideal gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$), $K = C_{\text{ads}}/C_{\text{eq}}$ and T is the temperature (K). ΔH° and ΔS° values can be obtained from the slope and intercept respectively, of Van't Hof plots of $\ln K$ versus $1/T$ (Jimoh *et al.*, 2015).

Optimization

For optimization, the following parameters were optimized using Design expert. Including: 1). Concentration 10-100 ml/L 2). Adsorbent Dosage 0.01-0.05g 3). pH 4-10 and 4). Contact Time: 3 hours. At various design conditions.

Preparation of Cr Solution

$\text{K}_2\text{Cr}_2\text{O}_7$ were dissolved in 1liter volumetric flask using deionized water to make 1000ml/L of Cr standard solution where serial dilution were made for other concentration 5.7g

RESULT AND DISCUSSION

FTIR Analysis of MIL-53

MIL-53 - FTIR (KBr, cm^{-1}): O-H (3590), C-H (3020), C=O (1790, 1705 & 1650), C-O (1250 & 125) and Fe-O (530). Figure 1.

The FT-IR spectrum of MIL-53 displayed a characteristic band at 3590 cm^{-1} were due to the stretching vibration of the O-H bonds from the surface absorbed water, which is less intense in the dehydrated form, as presented in Figure 1. The absorbance band at 1705 & 1692 cm^{-1} indicates the stretching vibration of (C=O) bonds found in COO^- .

The peaks at 1250 cm^{-1} and 1125 cm^{-1} were symmetric and asymmetric stretching vibrations of C-O pertaining to the carboxylate groups confirmed the presence of the ligand within the sample. The hydrated form shows a band at 863 cm^{-1} due to the bridging hydroxyl group (Fe-O(H)-Fe) (Costentin. C *et al.*, 2015), and the peak at 530 cm^{-1} corresponds to the vibration peak of n (Fe-O) which is also consistent with that of the literature (Nivetha, R *et al.*, 2019).

TGA-DTA Analysis

Figure 2, shows the thermogravimetric analysis (TGA) curve of MIL-53 measured in the air atmosphere and temperature up to 1000°C . The sample was thermally stable after heating to 340°C ; in the temperature range 350 – 510°C , the dehydration and decomposition process takes place. The DTA curve shows three exothermic peaks around 375°C to 500°C . In the TGA graph, there were weight loss at the first DTA peak. The first stage of thermal decomposition was observed and corresponds to the release of water molecules (mass loss 45 wt%). whereas the second DTA peak around 400°C was associated with a small weight loss of about 30%. This weight loss may be due to the decomposition of carboxylate from the sample and exothermic nature of the peak thought to occur from oxidation of the sample

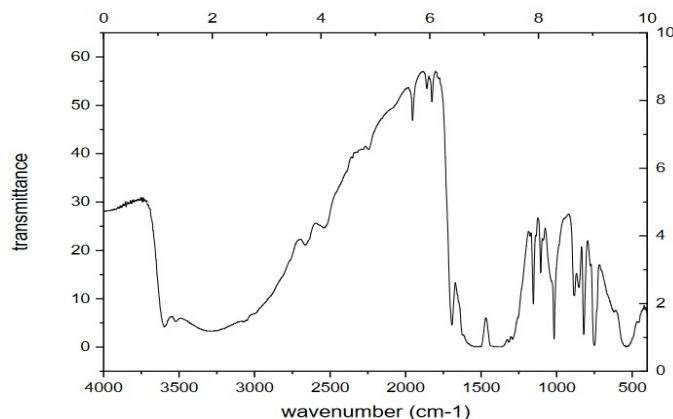


Figure 1. The FT-IR spectrum of MIL-53

The complete decomposition of the sample around 500 to 900 °C, indicating its decomposition and the gradual transition to metal oxide (Mayedwa, *et al.*, 2017).

Adsorption/desorption isotherm Analysis

Figure 3 shows the N₂ adsorption/desorption isotherm of the synthesized MIL-53. The isotherm analysis showed type I isotherm at 77 K with no hysteresis phenomenon. The calculated BET surface areas were (85.98, 167.72 and 277.40) m²/g for

MOF-53. In the low relative pressure region, the adsorption curve of all the samples increases sharply indicates the presence of micropores. The adsorption curve reached a plateau after that, indicate that most of the MOF porosity were attributed to the micropores (Waheed, *et al.*, 2024). The calculated surface area, volume of the micropores and average pore were (167.72) m², 0.055cm³/g and 2.820 nm for MOF-53.

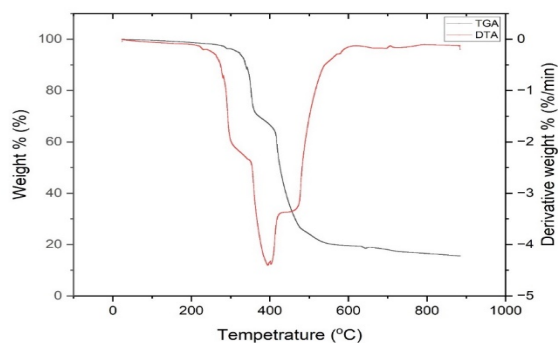


Figure 2. Shows the TGA and DTA curves for the synthesized MIL-53

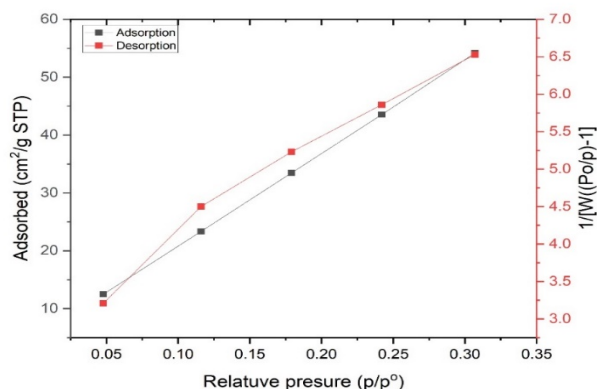


Figure 3. 77 K N₂ adsorption isotherm of MOF-53.

Pore size distribution

Figure 4 shows the pore size distribution of synthesized MIL-53. The average pore diameter were (1.820, 2.820 and 2.780) nm for MIL-53, more than 80% of the pores are micro-pores. The adsorption isotherms of N₂ on MIL-53 reveal intriguing

behavior, particularly its high adsorption capacity at low partial pressure. However, within a wide range, the adsorption amount exhibits only insignificant changes until reaching saturation pressure, where it rapidly increases, as presented in Figure 4.

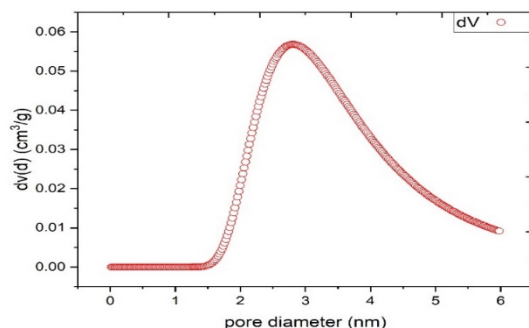


Figure 4. Porosity characteristics of the MIL-53

XRD Analysis

Figure 5, shows four typical XRD pattern of MIL-53, an intense diffraction peak from 25° to 29.2° centered, and at approximately 51.8° to 69.5°, peaks can be attributed to reflections from crystalline planes (100), (002), (111) and (202), (020), (311) of MIL-53 indicate the amorphous nature of the compound powder. The broad peaks indicate an amorphous structure with a large surface area. The result demonstrated high intensities at low degrees; however, the main diffraction peaks still maintained the same structure (Vu *et al.*, 2015), therefore the MIL-53 (Fe) crystal structure fully developed. The samples show a high crystalline phase (Qian *et al.*, 2013).

SEM-EDX Analysis

The SEM micrographs of MIL-53 revealed highly porous structure. A coarse morphology can be observed from Figure 4.31a-c. The morphological analysis clusters with irregular shapes, flakes of MIL-53 was observed (Noorani *et al.*, 2023). The prepared MOF was slightly irregular in a hollow spherical shape with pores and high degree of accumulation. The EDX spectrum of MOF-53 shown in Figure 6, reveals that the EDX spectrum of Mil-53 contains all four elements (C, O, Fe, Cl) of MOF-53. The weight % of carbon, oxygen, iron and chloride are 2.23%, 20.02%, 75.65% and 2.00% respectively, which indicates successful synthesis of MIL-53 (Fiaz K 2021)

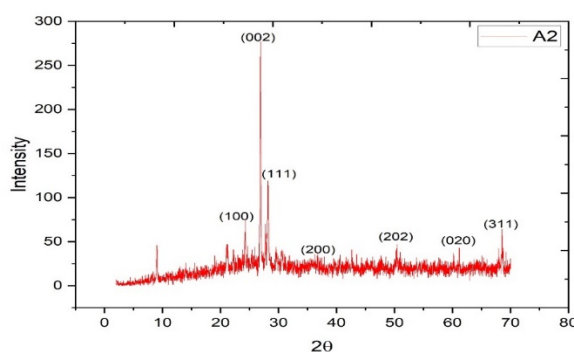


Figure 5. X-ray diffraction spectra of MIL-53

The FT-IR Analysis of Functionalize MIL-53

The FT-IR spectrum of amine, sulfonic and cyano functionality of MIL-53 displayed characteristic bands from 3406 to 3428 cm⁻¹ for all the study MOFs, this is due to the broad stretching vibration of

the O–H bonds from the surface absorbed water, which is less intense. The C≡N stretches bands of cyano group of MIL-53+CN appears as a sharp and intense bands at 2193 cm⁻¹. The vibration bands appeared at 1650-1552 cm⁻¹ were assigned to the

carboxylic functionality of MIL-53+CN, and can be attributed to C=O stretching. vibration of the

carboxylate group and the C-O stretch appears at 1108 cm^{-1} , as presented in figure 6.

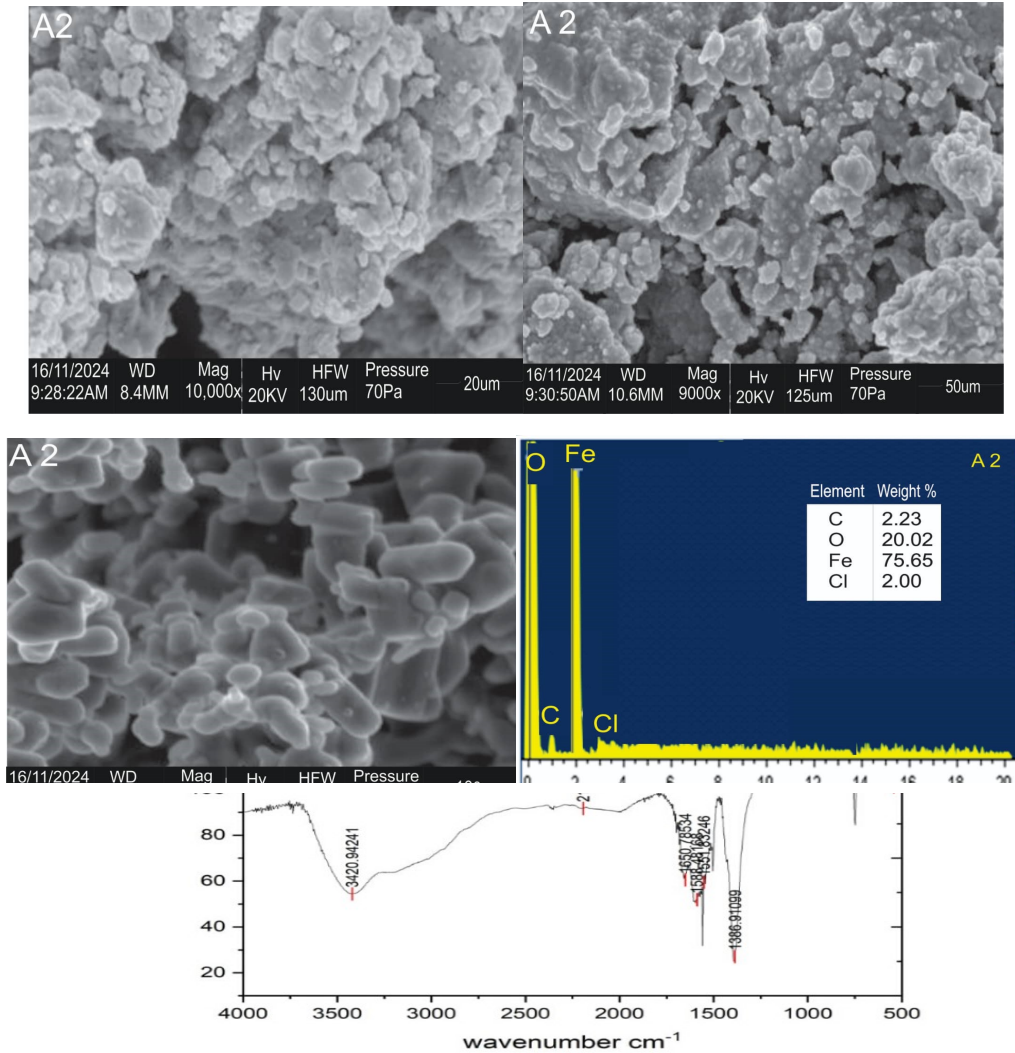


Figure 6. FT-IR spectrum of cyano functionality of MIL-53

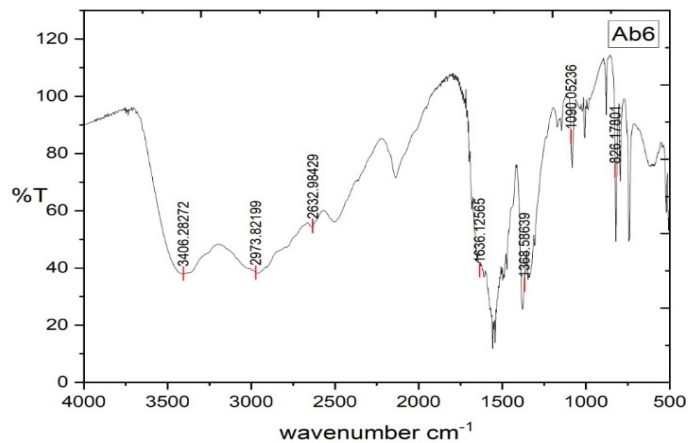


Figure 7. FT-IR spectrum of amine –MIL-53

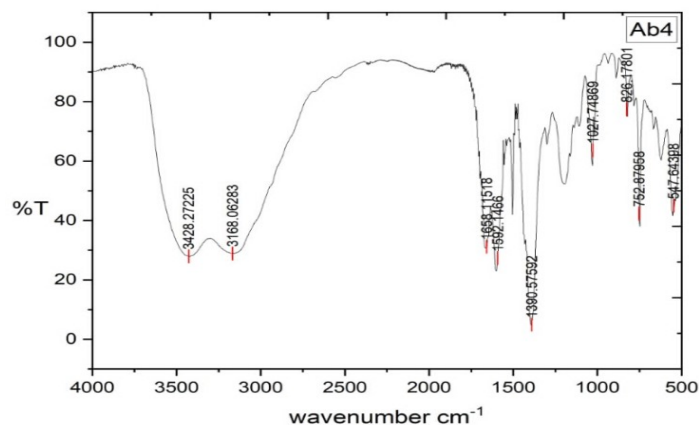


Figure 8. The FT-IR spectrum of sulfonic functionality MIL-53

Adsorption Study

Table 1, shows the Cr (III) adsorption analysis of functionalize MIL-53, the initial Cr (III) metal ion concentration were 0.099 ± 0.0014 , 0.098 ± 0.0028 and 0.118 ± 0.0014 ppm for MIL-53+SO₂H, MIL-53+NH₂ and MIL-53+CN respectively. It was observed that the adsorption capacity (q) of the studies MOFs were influenced by the Cr (III) metal ion concentration. Increase in concentration increases the quantity adsorbed by the MOFs. The adsorption capacity of the functionalize MIL-53 adsorbent were 59.00, 55.75, 49.00 and mg/g for MIL-53+CN, MIL-53+SO₂H, MIL-53+NH₂ and respectively. MIL-53+CN adsorbent has the highest adsorption capacity (q_e values) of 59 mg/g, followed by MIL-53+SO₂H (55.75) mg/g while MIL-53+NH₂ adsorbent has the lowest adsorption capacity of 49.00 mg/g. The adsorption capacity of MIL-53+CN adsorbent could

be as a result of the pore size or increase in the electrostatic interaction between the metals and the absorbent active sites. Moreover, this can be explained by the fact that more adsorption sites were being covered as the metal ions concentration increases (Mayedwa, *et al.*, 2017). The adsorption behaviour of Cr (III) metal ions were excellent, where the removal efficiency was over 90 - 99.9% when the initial concentration of Cr (III) ions was as low as 0.066 ppm. Trivalent Cr(III) is a target heavy metal contaminant in water environment, though its toxicity is less than Cr(VI). Several study on MOFs adsorption have been reported (Saleem *et al.*, Saleem *et al.*, 2016) used modified UiO-66-MOF for adsorption of Cr(III), and the best adsorption performance was obtained (67.3 mg g⁻¹) which was similarly compared to the studied MIL-53 in this study.

Table 1. The initial metal ion concentration and adsorption capacity of MIL 53 adsorbent

MIL 53 samples	Initial Concentration (mg/L)	Adsorption capacity q(mg/g)
	Cr (III)	Cr (III)
MIL-53+ SO ₂ H	0.1115 ± 0.0021	55.75
MIL-53+ NH ₂	0.098 ± 0.0028	49
MIL-53+CN	0.118 ± 0.0014	59

CN = cyano, SO₂H = sulfonic and NH₂ = amine

Thermodynamics study

The results obtained from the thermodynamics study were shown in Tables 2. The enthalpy ΔH of all the studied functionalized MIL53 were positive, the positive value of heat of adsorption (ΔH) signifies an endothermic reaction for all the studied samples, which indicate a favorable adsorption process for all the studied samples. MIL-53+NH₂ for Cr (III) adsorption has the lowest value of ΔH , which suggests that the adsorption process is likely to be physisorption (Hema *et al.*, 2007). All the studied samples have a positive values of ΔS , except MIL-53+SO₂H absorbent, the negative value of entropy

shows the decreased degree of disorder of the adsorption system, which is caused by the range of Cr ion movement being restricted by the adsorbent solid surface after the adsorption(Xiang *et al.*, 2017). The positive values of entropy ΔS are an indication of an increased disorderliness and randomness at the adsorbent-sorbate interface and affinity for adsorbent material (Lawal OS *et al.*, 2017). The Gibb's free energy values indicate the degree of spontaneity of the sorption process. At 318 and 328K, the ΔG value of MIL 53 for Cr (III) adsorption were negative, confirming the thermodynamic feasibility of adsorption of Cr (III) on the samples framework

(Chowdhury *et al.*, 2011). While at 308K, the ΔG value of MIL 53 for Cr (III) adsorption were positive, indicating non-spontaneous process at this

temperature. Hence, need to improve the adsorbing capacity, at low temperature.

Table 2. The thermodynamics analysis of the adsorption of Cr (III) metal ion

MOF samples	ΔH KJ/Mol	ΔS KJ/Mol	ΔG KJ/Mol		
			308K	318K	328K
MIL-53+SO ₃ H	64914.779	-209.010	539.514	-1880.591	-3640.697
NH ₂ @MIL-53	114503.162	367.628	1273.436	-2402.853	-6079.143
MIL-53+CN	133102.027	428.139	1234.991	-3046.406	-7327.803

Optimization Reaction Conditions for Adsorption of Cr (III) by MIL53

The adsorption optimization of the studied samples were carried out using Box-Behnken Design (BBD) module in response surface methodology (RSM) to discover the best adsorption process for Cr (III) metal ions. RSM aims to decrease the number of experimental runs required to obtain satisfactory information for statistically agreeable results (Jumaah *et al.*, 2022). The BBD was applied using Design Expert with total number of seventeen experimental runs. The empirical model was created utilizing three optimization parameters as independent variables (concentration, pH, and dosage) production as the response (dependent variable). The combined impacts of the independent factors were studied.

The experimental data acquired from the suggested reaction conditions presented by BBD model. From the experimental data, it was inferred that the amount

adsorbed in all seventeen (17) experiments for all the studied samples at different conditions were within the range of 79.01 – 94.26 mg/g. CN+MOF-53 has the highest adsorption of 94.26 mg/g, SO₃H+MOF-53 has 92.60 mg, while NH₂+MOF-53 has the lowest adsorption of 79.01 mg/g.. Figure 9 - 11, shows the predicted vs. actual plot adsorption of all the study MOFs for Cr (III) ion, there is a close distribution of data points between the actual experimental and predicted amount adsorbed along the straight line of the plot, demonstrating excellent correlation between these values and confirming that the model adequately predicts the response variable in actual values (Ocholi *et al.*, 2018). Thus, an increase in concentration (A) and dosage (C) will result in a significant increase in the samples percentage yield, while an increase in pH (B) will lead to a decrease in the percentage yield.

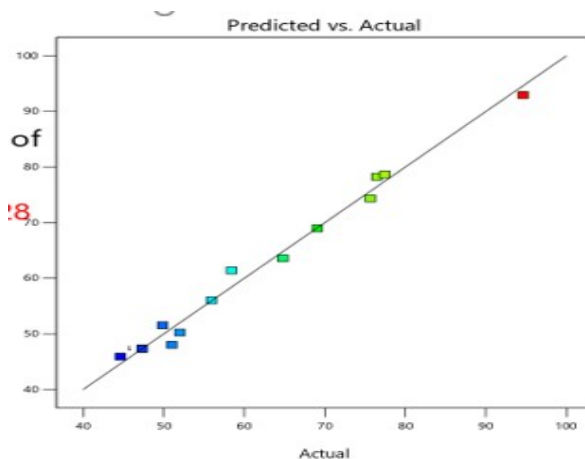


Figure 9: Graph showing predicted versus actual value for MIL-53+SO₃H for Cr (III) adsorption

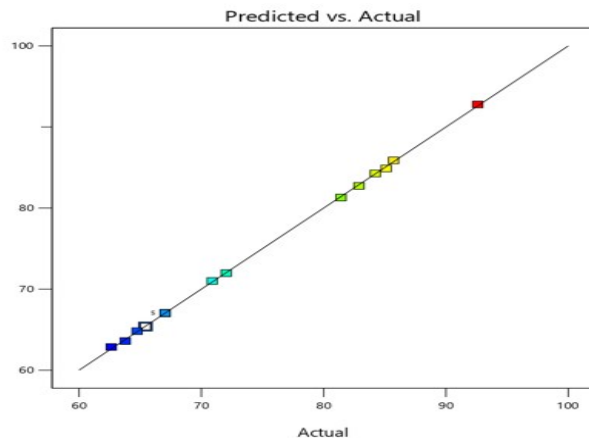


Figure 10: Graph showing predicted versus actual value for MIL-53+NH₂ for Cr (III) adsorption

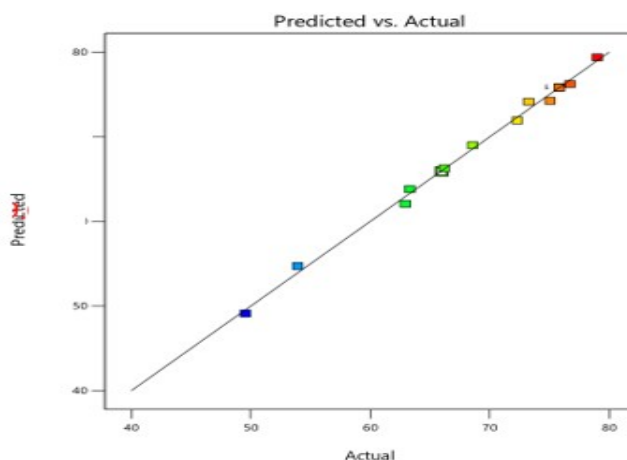


Figure 11: Graph showing predicted versus actual value for MIL-53+CN for Cr (III) adsorption

The ANOVA Quadratic model of MOFs for adsorption of Cr (III) ions

The ANOVA Quadratic model for all the studied MIL-53 for both Cr (III) adsorption. The Model F-value of Cr (III) adsorption are 72.97, 4445.52 and 223.06 for MIL-53+SO₃H, MIL-53+ NH₂ and MIL-53+CN, respectively. All the model F-value of the study MOFs implies the model are significant. Also, the p-values were less than 0.0500, indicate model terms are significant. In this case A, B, C, AB, AC, BC, A², B², C² are significant model terms. Values (concentration, pH and dosage) on the adsorption yield was investigated while one of the input variables was fixed and depicted in Figures 12 to 14 for all the study samples. The amount adsorbed of Cr (III) ion was

For Cr (III) Adsorption

Effect of concentration and pH (AB) on Adsorption

The 3D response surface plots for this combined effect were described as Figures 12a-c, from the surface plots, it was deduced that high adsorption

greater than 0.1000 indicate the model terms are not significant. Where A, B, and C stand for concentration, pH, and dosage, respectively, the direct linear impacts of the independent process variables are represented by the coefficients A, B, and C. As opposed to AB, AC, and BC, which represent the linear interaction effects between molar ratio/temperature, molar ratio/time, and temperature/time, respectively, and A², B² and C² which depict the quadratic impacts of the independent process variables. yield was achieved at a high concentration and above pH 6. Therefore, in this study, an optimum percentage of yields could only be achieved at a high concentration and a pH above 6. Subsequently, these result confirms the ANOVA result, which shows that the combined effect of AB was significant with a p-value less than 0.005 (< 0.0001) and (<0.005). The AB significant (P-value) of MIL-53 were 0.1134, (< 0.0001) and (0.0002), which are significant except MIL-53+SO₃H.

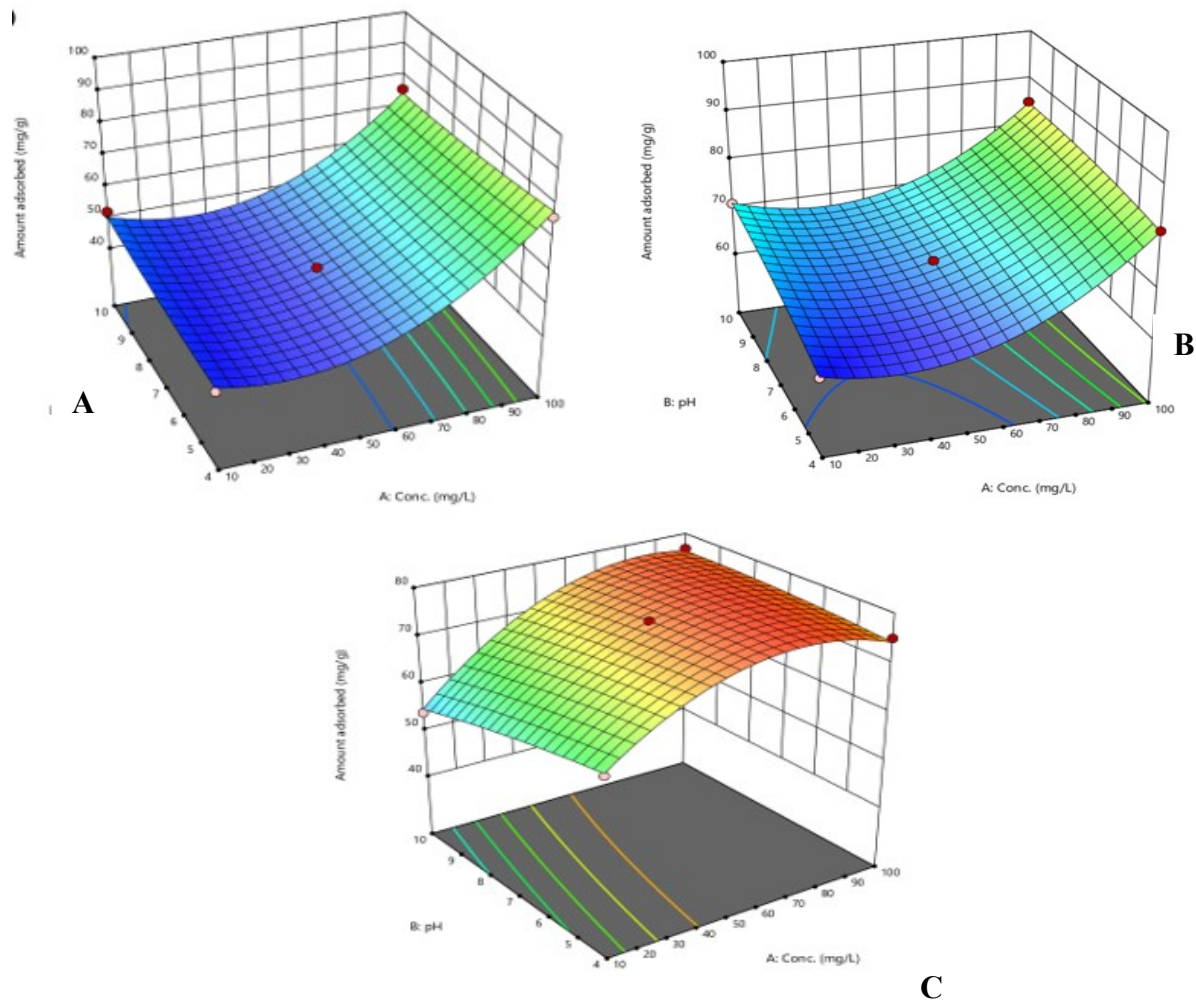


Figure 12: Graph between concentration and pH a). MIL-53+SO₃H, b). MIL-53+NH₂ and c). MIL-53+CN

b) Effect of concentration and dosage (AC) on Percentage Yield

Figure 13a-c, reveal the 3D response surface plots, a high adsorption yield could be obtained at a high concentration and low dosage of (0.03 g). Thus, in this study, an optimum percentage of adsorption could be achieved at high concentration and low dosage. The ANOVA result shows that the combined effects of AC were significant with a p-value less than (< 0.0001) for all the studied samples, except MIL-53+SO₃H which was 0.6374 and not significant.

c) Effect of pH and dosage

Figures 14a – c, depict the 3D for this effect that the highest adsorption yield was obtained at a low temperature and either low or high reaction time. Eventually, lower adsorption were observed with low pH and low dosage. This agreed with the conclusion from the ANOVA result, which indicate that the interaction effect of BC were significant for all the studied samples, with p-value less than (0.005), except MIL-53+SO₃H which was 0.0110.

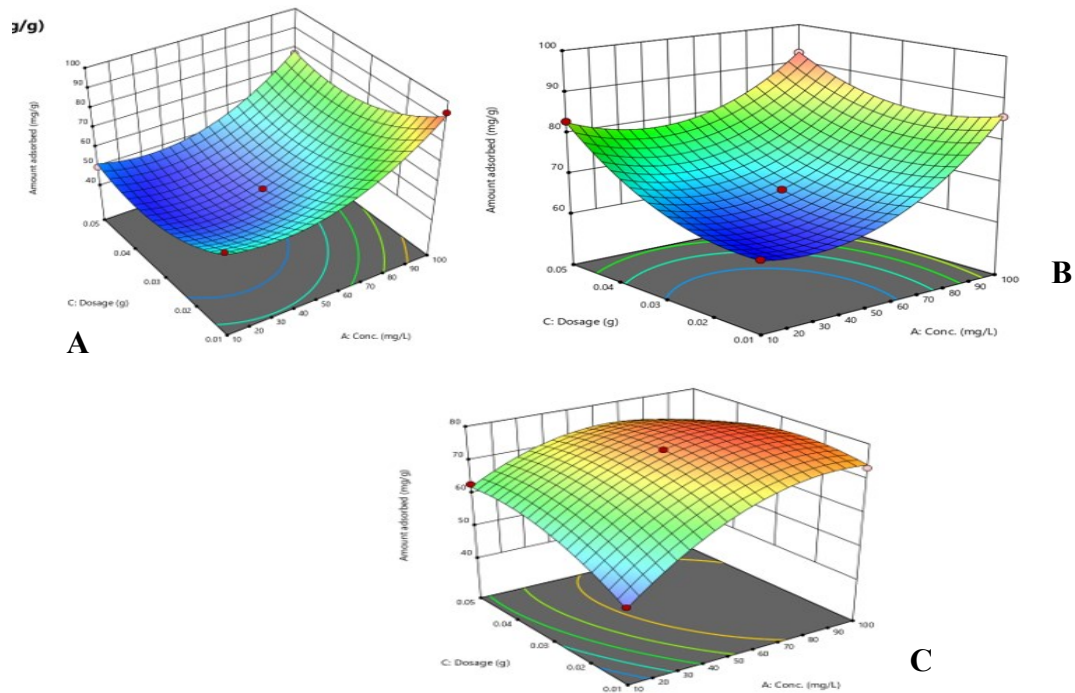


Figure 13: Graph between concentration and dosage a). MIL-53+SO₃H, b). MIL-53+NH₂ and c). MIL-53+CN

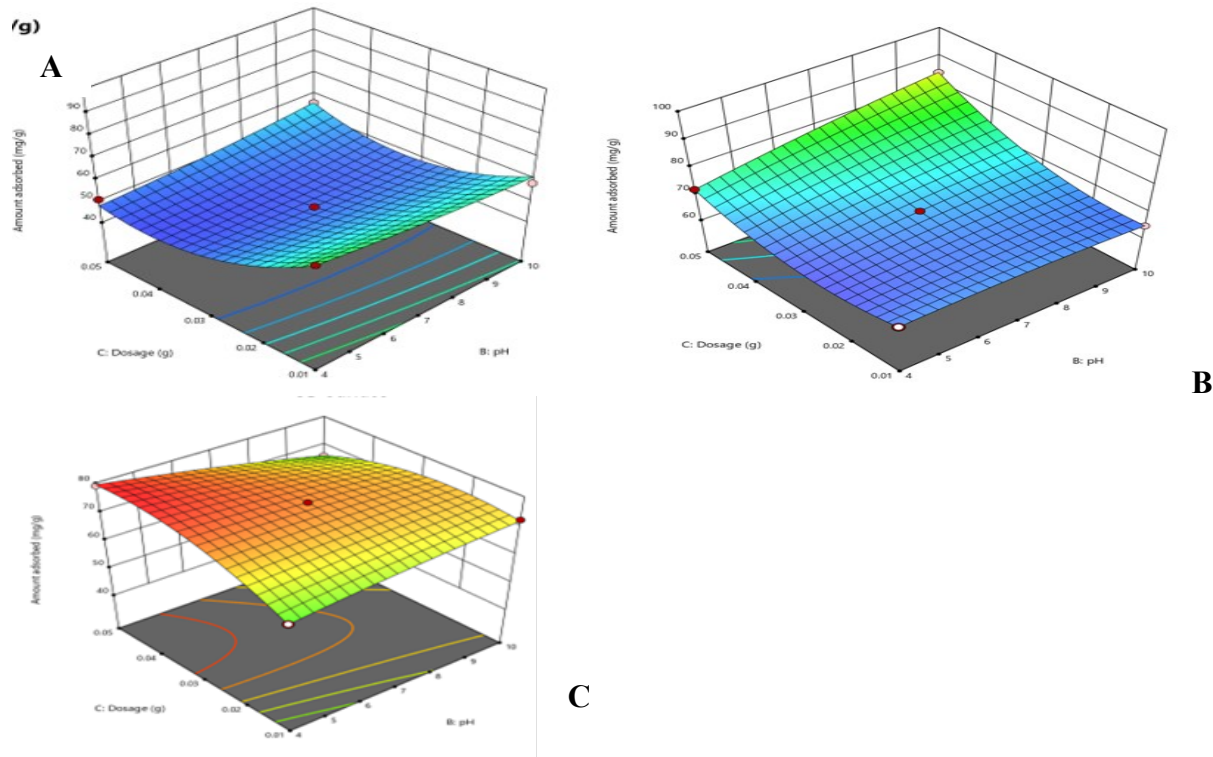


Figure 14: Graph between dosage and pH a). MIL-53+SO₃H, b). MIL-53+NH₂ and c). MIL-53+CN

Conclusion

The study based on the synthesis and characterization of functionalized MIL-53 with amine (MIL-53+NH₂), sulfonic (MIL-53+SO₃H) and cyano (MIL-53+CN) as a novel adsorbents for selective removal of Cr(III) ion from aqueous samples. MIL -53+CN adsorbent has the highest adsorption capacity (q_e values) of 59 mg/g, followed by MIL-53+SO₃H (55.75) mg/g while MIL-53+NH₂ adsorbent has the lowest adsorption capacity of 49 mg/g. All the studied samples have positive values of ΔS, except MIL-53+SO₃H adsorbent, The Gibb's free energy values indicated that the degree of spontaneity of the sorption process. The BBD-based RSM revealed the effective quadratic regression polynomial model, with variables A (concentration), B (pH) and C (dosage) having more significant effect on this process.

Reference

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