Facile Synthesis of Hierarchically Structured MIL-53(Al) With Superior Properties Using An Environmentally-Friendly Ultrasonic Method For Separating Lead Ions From Aqueous Solutions

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Facile synthesis of hierarchically structured MIL-53(Al) with superior properties using an environmentally-friendly ultrasonic method for separating lead ions from aqueous solutions

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Abstract

The present study aims to investigate novel ultrasonic synthesized MIL-53(Al) and its applications in adsorption. Both conventional and ultrasonic methods were used to synthesized Mil-53(Al). The ultrasonic-assisted synthesis procedure results in reducing synthesis time to 24 hours; however, Compared to that conventional method takes 3 days to create the framework. Applying ultrasonic waves also increases surface area to 50% more than the ones synthesized by the conventional method, as well as creating the hierarchical MIL-53(Al) structure (meso- and micro-) pores. To this end, XRD, FESEM, BET, and FTIR analyses were employed to identify and characterize MIL-53(Al). The unique structure and high MIL-53(Al) yield lead to effective adsorption among MOF and lead ions. The optimum conditions for removing lead were 6.0 pH, 20 mg/l concentration, 60.0 min contact time, 0.04g adsorbent dose, and 318k temperature with 97.63% removal of the lead ions. The experimental adsorption equilibrium and kinetic data fitted the Langmuir isotherm and pseudo-second-order kinetic models, respectively. Moreover, the use of ultrasonic synthesized MIL-53(Al), for the first time as a novel adsorbent in heavy metal removal, pointed to the great potential of this new environmentally-friendly adsorbent in removing lead ions from aqueous solutions.

Introduction

Due to the fast development of trade 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 attention¹. Among all heavy metals, lead is one of the most toxic elements. Lead is used as a significant raw material used in many industrial production operations such as batteries, radiation devices, solar cells, ceramics, and paint industries. Lead can cause nervous disorders such as IQ decline. In addition, it causes anemia and further side effects such as autoimmunity², headache, insomnia, liver and kidney problems, gastrointestinal, and nervous system disorders, to name a few^{3,4}. Therefore, Pb (II) decontamination of the contaminated water before being discharged into the water reservoir from industrial plants is of high significance.

A number of techniques such as adsorption, chemical precipitation, coagulation, membrane filtration, ion exchange, electro-reduction are employed to remove heavy metals from wastewater. Compared to other techniques in water treatment, adsorption is a more appropriate option because of its simplicity, efficiency, and economy^{5,6}.

Different adsorbents have been developed to remove dissolved materials from the solution using ion adsorption mechanisms. In this regard, preparing a promising adsorbent is considered a significant challenge. Nano-porous compounds such as Metal-Organic Frameworks (MOFs) have received significant attention in recent years due to their vast contact surface areas, solvent stabilities, high porosity, well-organized pores, and regular particle size⁷⁻⁹. Further, MIL-53 is a group of MOFs produced by the Lavoisier Institute, which is a white powder with the chemical formula of $[Al(OH)[(O_2C)-C_6H_4-(CO_2)]$. Owing to the unique surface area, porosity, pores shape, size tunability, and adsorptive nature, MIL-53(Al), among the MILs family, can efficiently stimulate the scientific society^{10,11}. MOFs are used in different fields such as catalysis, separation, gas storage, and drug delivery. Few studies have been conducted on their applications as the adsorbents used for removing hazardous substances such as volatile organic compounds and dyes from aqueous solutions¹²⁻¹⁴. The adsorption performance depends mainly on several characteristics such as crystallization, particle size, and availability of the functional groups. Since smaller particle sizes have additional surface availability, they cause higher adsorption capacity.

In the present study, MIL-53(Al) was synthesized through a novel environmentally-friendly method using ultrasonic waves to enhance the energy efficiency of material synthesis, decrease the reaction time and even temperature. The method mentioned above will also increase the surface area of the adsorbent, which will contribute to a promising adsorbent that is a time and energy consumer to form a framework and boosts the adsorbent features in order to remove lead ions from aqueous solutions. Moreover, this study employed the adsorption technique to eliminate lead ions from the solution. This technique was also investigated using the kinetic and isotherm approaches. Of note, the effects of solution temperature, pH, and adsorption dosage on removal efficiency were tested.

Materials and methods

Materials and reagents

The primary materials used in the synthesis and adsorption tests were of analytical reagent grade. Aluminum (III) nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and 1,4-BenzenediCarboxylic (BDC) acid were used as Al(metal) sources and organic ligands, respectively, which were purchased from Merck, Germany. In addition, N, N-Dimethylformamide (DMF), methanol (CH_3OH), Hydrochloric acid (HCl), and sodium hydroxide (NaOH) were acquired. Moreover, the source of lead ions was $[\text{Pb}(\text{NO}_3)_2]$ procured from Merck, Germany. Deionized (D.I.) water was used to prepare all solutions.

Preparation of hierarchically structured MIL-53(Al)

The present study employed a new environmentally-friendly method for ultrasonic-assisted synthesis (UAS) of MIL-53(Al). According to this method, (6.5 g) Aluminum (III) nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) (98% purity) and (1.44 g) 1,4-BenzenediCarboxylic (BDC) acid (98% purity) with 25 ml of D.I water were stirred for 10 minutes at room temperature until complete dissolution is achieved. The mixture was then exposed to ultrasonic waves of 24 kHz and 100% intensity for 30 minutes after dissolving and then, it was transferred to 100 ml autoclave with black Teflon liner steel. Finally, an oven was used to heat the sample to 220°C for 24 hours. The autoclave was cooled down. Then, the solid phase was separated using a centrifuge, and 35 ml of DMF solution (solid solvent) was added to remove unreacted terephthalic acids trapped in the pores of the samples. The autoclave was put back in the oven to be

heated to 150°C for 12 hours. Finally, the solid phase was separated by centrifuge and washed with methanol; then, 40 ml of methanol was added to the sample, and the sample was dried in an oven at 150 ° C overnight. The result is a solid white powder subjected to different analyses used for identifying and ensuring the correct formation of MIL-53 (Al). In the end, the synthesized crystals were calcined at 650K in the air for 5 h. In order to synthesis MIL-53(Al) with the conventional (CS) method, the primary mixture, including water, BDC, and Aluminum(III) nitrate nonahydrate with the same amount as ultrasonic synthesis, was stirred for 1 hour at room temperature until complete dissolving and then transferred to 100 ml autoclave with black Teflon liner steel and used the oven to heat the sample to 220°C for 72 hours. The autoclave was let to be cooled down; all the other experimental conditions took place the same as the ultrasonic synthesis method.

Characterization

The morphology and composition characteristics of MIL-53(Al) were evaluated using Field Emission Scanning Electron Microscopy (FESEM) and a Seron AIS2100. In addition, X-Ray Diffraction (XRD) was employed to examine the crystalline structure recorded by the PW1730 diffractometer with $\lambda_{\text{CuK}\alpha}=1.54056 \text{ \AA}$ and a step size of 0.05 at 40 kV and 30 mA. The BELSORP MINI II instrument measured the Brunauer-Emmett-Teller (BET) analysis within the nitrogen adsorption-desorption isotherm method at (77k) in order to detect structural properties of MIL-53(Al). Fourier-Transformed Infrared spectroscopy (FT-IR) was obtained using the PERKIN EKMER instrument at a resolution of 400–4000 cm^{-1} . Further, AAS was used to measure the lead concentration using Model 3110 Perkin Elmer Atomic Absorption Spectrometer. The pH meter model, combined with a pH electrode, was of the 827 pH Lab (Metrohm, Swiss).

Preparation of lead solutions

Millipore/D.I. water and lead (II) nitrate were used to prepare the lead stock solution with a concentration of 1000.0 mg/L. Other lead solutions with different concentrations were freshly prepared for each experiment using the stock solution.

Evaluation of Adsorbents Performance

MIL-53(Al) adsorption capacities for Pb(II) were presented at different dosages with known initial concentrations for fixed values of time, temperature, and pH. When the solution reached equilibrium, two solid and liquid phases were divided through filtration and then, Atomic

Absorption Spectrometer (AAS) was employed to determine the remaining concentration of the Pb ions in the solution. The pH of point of zero charges (pHpzc) of MIL-53(Al) was calculated by the method proposed by Faria et al.¹⁵. The effect of initial pH on lead ion adsorption was also examined at different pHs ranging from 2.0 to 7.0. The pH of the solution was fixed by adjusting HCl and NaOH 0.1 and 0.01 M to the solutions. Then, 0.04 g of MIL-53(Al) was added to every 40 ml of solution, and the agitation samples were placed on an incubator shaker at a speed of 315 rpm for three hours and at room temperature. Eventually, the final concentration of lead ion was analyzed using AAS.

Further, Pb adsorption isotherm and other practical parameters were studied in the following experimental conditions: the concentration of 10–130 (mg/L), time range of 3.0–180.0 min, and different temperatures of 288, 298, 308, and 318 K. The adsorbent dosage ranges from 0.001 to 0.04g. The kinetics investigations for Pb(II) removal were evaluated through the analysis of Pb adsorption in different time periods. The rates of metal ions (R%) removal and removal capacity of Pb(II) q_e (mg/g) were determined using equation (1) and equation (2), respectively¹⁶:

$$Removal\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e(mg/g) = (C_0 - C_e) \times \frac{V}{m} \quad (2)$$

In which V(ml) is the volume of lead ion solution; m(g) is the amount of MIL-53(Al); and C_0 and C_e are the initial and equilibrium concentrations (mg/L) of lead ion adsorbed, respectively.

Result and discussion:

MIL-53(Al) characterization

The XRD pattern of the synthesized MIL-53(Al) is presented in Figure 1. These patterns are very similar to the previous one reported in reference¹⁷. The XRD pattern of the UAS and CS MIL-53(Al) in this study shows the prominent characteristic peaks at $2\theta = 9.38^\circ$, 12.58° , 17.93° , 23° , 48° , 25.28° , 27.33° , which match the peaks reported in the literature¹⁷, indicating that MIL-53(Al) is well crystallized and synthesized. Also, the difference in peak intensities is due to higher

ultrasonic energy as a driving force, increasing nucleation rate and leading to a considerable amount of cavitation bubbles¹⁸.

Figure 1. X-ray diffractograph of the ultrasonic and the conventional synthesized MIL-53(Al).

The morphology of UAS and CS MIL-53(Al) samples with different magnifications were examined using FESEM, the results of which are presented in Figure 2. According to this figure, the samples synthesized through the sonochemical method have octahedral shapes with crystal-like structures. Such structures are not aggregated; instead, they have a more uniform particle size which is smaller than the sample obtained by the conventional hydrothermal method. According to the standard conditions required for MOF crystal growth, faster nucleation rates result in smaller crystal sizes¹⁹. Following the FESEM characterization results, the sonochemical synthesized MIL-53(Al) has smaller uniformly distributed nanoparticles mainly because of the accelerated nucleation and shorter synthesis time required for sonochemical synthesis.

Figure 2. FESEM images of the ultrasonic-assisted and the conventional synthesized MIL-53(Al) at different magnifications.

The N₂ adsorption-desorption isotherm of MIL-53(Al) is exhibited in Figure 3. The synthesized sample resembles an IOPAC-type IV isotherm with a type H4 hysteresis loop, illustrating hierarchical structure including mesoporous and microporous in the sample. While conventional synthesis MIL-53(Al) only possesses a microporous structure²⁰. Furthermore, BET data of MIL-53(Al) are given in Table 1. The high crystallinity and porosity of the sample yield a high BET

surface area of 1538.6 m²/g and a vast average pore size of 1.74 nm. BET surface area and average pore size are greater than those conventionally synthesized MIL-53(Al) introduced in the literature^{20–22}; it could be explained by the effect of ultrasound waves on the crystalline structure of MIL-53(Al). Ultrasonic intensity as a driving force ends up in a substantial quantity of cavitation bubbles, and increases in crystallinity, leading to a higher BET surface area in line with the XRD pattern discussed^{18,23}. Moreover, the high intensity of ultrasonic waves creates mesopores in the structure of MOFs²⁴, leading to a hierarchical ((meso- and micro-) pores) structures attending to a more significant average pore sizes^{20,25}.

Figure 3. *N₂* adsorption-desorption isotherm of ultrasonic synthesis MIL-53(Al)

Sample	BET Surface area (m ² /g)	Pore volume ¹ (cm ³ /g)	Average pore size (nm)	External surface area ² (m ² /g)	Mesopore volume ³ (cm ³ /g)	Micropore volume ² (cm ³ /g)	Ref.
UAS MIL-53(Al)	1538.6	0.671	1.7443	20.22	0.07	0.600	This study
CS MIL-53(Al)	1274.3	0.560	1.755	5.88	0.027	0.533	This study
MIL-53(Al)	1184	-	-	-	0	0.45	²⁰
MIL-53(Al)	1073	0.46	-	-	-	-	²¹
MIL-53(Al)	1027	0.56	0.66	-	-	-	²²

Table 1. BET characteristics of MIL-53(Al).

¹ Measured using t-plot method.

² Measured using t-plot method.

³ Mesopore volume(From BJH model) = Totalpore volume– Micropore volume.

Figure 4 illustrates the FT-IR spectrum of the synthesized UAS MIL-53(Al) which also shows the vibration bands in the wavelength range of 1700-1400 cm⁻¹, indicating that the carboxylic functional groups are attached to aluminum. According to this figure, the firm observed peaks at 1507.87 and 1579.56 cm⁻¹ belong to the (–COO) asymmetric stretching, and the characteristic peak at 1413.15 belongs to (–COO) symmetric stretching of the carboxyl vibration. No additional peak is observed at a wavenumber of 1700 cm⁻¹, indicating that the free BDC acid molecules are completely removed from UAS MIL-53(Al) pores¹⁷. The peaks at 1631.9 cm⁻¹ and vibration bands ranging from 3700 ± 3400 cm⁻¹ confirm the observation of the bending and stretching modes of water as well as the signature of the hydroxyl group that links the aluminum particles ²⁶. The FTIR bands were considerably similar to the FTIR of US MIL-53(Al) samples from the standard MIL-53(Al)²⁶.

Figure 4. FT-IR spectrum of MIL-53(Al).

Adsorption parameters efficiency studies

Selectivity of nickel, copper, lead on US MIL-53(Al)

In order to discover the selectivity of UAS MIL-53(Al) in removing the heavy metals from water, an adsorption experiment was carried out to measure the remaining concentration of these metals such as pb^{2+} , Ni^{2+} , Cu^{2+} in the solution after adsorption. Three adsorption experiments, each containing 20 ppm of intended heavy metal, 0.03 g US MIL-53(Al), and 40 ml solution, were carried out to determine the selectivity of the adsorbent. According to the Figure 5, MIL-53(Al) as an adsorbent can perfectly remove lead from the solution since it comprises carbonyl groups. Therefore, the following tests were carried out using lead only.

Figure 5. US MIL-53(Al) selectivity of heavy metal ion's

(20 ppm of intended heavy metal, 0.03 g MIL-53(Al), and 40 ml solution, 298K temperature)

Effect of pH on adsorption rate

The pH of the mixture is considered an essential parameter to be examined during the adsorption studies since changing pH can alter the surface charge of the adsorbent. Also, pH can strongly influence the solubility of metal ion.²⁷ First, in order to choose the pH range of the solution, the pH_{pzc} of the adsorbent should be analyzed. The pH_{pzc} of the solution is at which the surface charge of the adsorbent is zero. In case $pH_{pzc} > pH$, the surface has a more positive charge by decreasing pH, and in case $pH_{pzc} < pH$, the surface has a more negative charge by increasing the pH. Figure 6 shows the pH_{pzc} in this study. The removal efficiency of Pb(II) ions was investigated in different initial pH ranges (2.0 to 7.0), as shown in Figure 7, which were set using the required amount of HCl or NaOH solutions. The pH range in this study was selected from (2.0 to 7.0) because at $pH \geq 7$, lead ions precipitated as $Pb(OH)_2$. While pH_{pzc} 's adsorbent charge, at pH above 5 is negative, it is positive at lower pH^{12,28,29}. As observed in Figure 7, upon increasing the pH from 2 to 7, at first, the removal of adsorption on UAS MIL-53(Al) increases from 19% to 86%, meaning that the surface charge of adsorbent is negative. Then pH of 7 causes Pb(II) to hydrolyze in aqueous solution resulting in a slight decrease in adsorption rate. Finally, the optimum pH is obtained at

6.0. Therefore, as pH increases, the attraction between Pb^{2+} and the opposing surface increases. As a result, the adsorption rate of lead ions increases upon reducing hydrogen ion concentration which competes with Pb^{2+} ions for the adsorbent sites. The additional parameters to be considered include initial Pb(II) concentration (20.0 ppm), contact time (60.0 min), volume of the solution (40 ml), adsorbent dosage of 0.04 g, and temperature of 298 K.

Figure 6. Effect of pH on the zeta potential of US MIL-53(Al) adsorbent

Figure 7. Effect of pH

(pH range (2-7), Pb(II) concentration (20.0 ppm), contact time (60.0 min), volume of the solution (40 ml), adsorbent dosage of 0.04 g, and temperature of 298 K)

Effect of adsorption dosage

The effect of UAS MIL-53(Al) dosage on Pb removal was studied in the range of 0.001 to 0.04 g. This study was conducted at a temperature of 298 K and pH of 6 with an initial Pb(II) concentration of 20 ppm for about 60 minutes. As shown in Figure 8, the adsorption rate of Pb(II) increases from 27.1% to 86% upon increasing UAS MIL-53(Al) dose, thus increasing the number of available adsorption sites on the UAS MIL-53(Al) surface for binding Pb(II) ions. The significance of the adsorbent dosage indicates its adsorption capacity at a specific initial concentration. It is expected that upon increasing the amount of the adsorbent, the adsorption efficiency will increase due to the increasing amount of adsorbent. Because of the large surface area of the sample, the number of active sites for complexing metal ions increases and the adsorption process accelerates³⁰. In case the adsorbent reaches its maximum efficiency, the number of active sites on the adsorbent surface corresponds to the number of metal ions available in the solution in the equilibrium adsorption process.

Figure 8. Effect of adsorbent dosage.

(pH of 6, Pb(II) concentration (20.0 ppm), contact time (60.0 min), volume of the solution (40 ml), adsorbent dosage range of (0.001 to 0.04g), and temperature of 298K)

Effect of initial concentration

The effect of the initial concentration of UAS MIL-53(Al) on the adsorption of Pb was examined in the range of 20.0-130.0 ppm at a temperature of 298 K and pH of 6. As shown in Figure 9, as the initial concentration of lead ions increases, the removal percentage for this ion decreases from 86% to 34.5%, mainly because the interaction between lead ions and the active adsorbent sites increases at low concentrations, thus leading to a high percentage of adsorption. However, due to the saturation of the adsorbent surface at higher concentrations, more metal ions remain unabsorbed in the solution and the adsorption efficiency decreases upon increasing the concentration. An increase in the concentration of the metal ion would increase the number of collisions between the metal ions and the adsorbent, stimulating the removal of the heavy metal. The number of adsorbed metal ions per adsorbent mass increases in this process. In addition, the adsorption capacity increases as a result of increasing the initial concentrations of metal ions in the solution.

Figure 9. Effect of initial concentration

(pH of 6, Pb(II) concentration range of (20.0-130.0 ppm), contact time (60.0 min), volume of the solution (40 ml), adsorbent dosage (0.04g), and temperature of 298 K)

Effect of temperature on adsorption rate

The adsorption rate of lead ions via UAS MIL-53(Al) was investigated in a condition characterized by an initial Pb(II) concentration of 20 ppm, pH of 6, 0.04 g of the adsorbent, and varying temperatures of 288, 298, 308, and 318 K. Figure 10 shows a comparison between the removal efficiency and temperature, depicting an increase in the amount of the adsorption while increasing temperature from 66.9% to 97.63% mainly due to the movement of lead ions and the consequent increase in the number of ions colliding with active sites. In addition, increasing the temperature can reduce the viscosity of the solution, which ultimately increases the penetration rate of the adsorbent molecule, hence an increase in the amount of the adsorption.

Figure 10. Effect of temperature

(pH of 6, Pb(II) concentration (20.0 ppm), contact time (60.0 min), volume of the solution (40 ml), adsorbent dosage (0.04g), and temperature range of (288 K-318 K))

Effect of contact time on adsorption rate

The effect of contact time on the adsorption rate of lead was investigated using 0.04 g UAS MIL-53 (Al) as an adsorbent in different time durations from 5 to 180 minutes under some other conditions such as initial Pb(II) concentration of 20 ppm, pH of 6, and temperature of 298 K. As observed in Figure 11, the adsorption percentage increases upon increasing the time. Finally, by occupying all the active sites on the adsorbent, the adsorption speed would decrease until reaching equilibrium. The changes occur rapidly in the first 30 minutes and the adsorption capacity increases fast. Then, its growth rate decreases considerably and reaches equilibrium in 60 minutes. Hence, the time limit decreases from 180 min to 60 min for all the other experiments. During the first 30 minutes of the adsorption, the process accelerates owing to the large number of adsorption sites available for metal ions. Over time, increased adsorption slows down due to such constraints as repulsive forces between the adsorbed metal ions on the surface of UAS MIL-53(Al) and metal ions in the liquid; of note, the adsorption sites remain intact. On the contrary, during the initial stages of adsorption, the adsorbent pores are filled by the adsorbed ions. In the latter stages of adsorption,

the metal ions are forced to move more profoundly and longer to capture the pores, thus reducing the adsorption rate within minutes. The adsorption process continues until reaching the equilibrium time for adsorption. Equilibrium time is defined as when the adsorption process reaches equilibrium and saturation and the adsorption rate does not change much with time.

Figure 11. Effect of time

(pH of 6, Pb(II) concentration (20.0 ppm), contact time range of (5.0-180.0 min), volume of the solution (40 ml), adsorbent dosage (0.04g), and temperature of 298K)

Adsorption isotherm

The adsorption isotherm models proposed by Langmuir³¹, Freundlich³¹, Temkin³¹ were applied at a temperature of 298 K with different lead concentrations of 20, 50, 70, 100, and 130 ppm, 0.04 g of UAS MIL-53(Al), and pH of 6 for 60 min to investigate the interaction between equilibrium concentration data and lead ion adsorption.

Langmuir isotherm

This isotherm is employed to adsorb a dynamic equilibrium surface on perfectly homogeneous surfaces, assuming a monolayer coating onto the adsorbent surface area. In addition, due to the

occupation of the adsorption sites, the adsorbed molecules do not interact with each other. The parameters of the Langmuir isotherm can be calculated through plotting its linear diagram in equation (3), as shown in the following:

$$\frac{c_e}{q_e} = c_e \frac{1}{q_m} + \frac{1}{k_l q_m} \quad (3)$$

where C_e (mg/l) is the metal ion concentration, q_e (mg/g) the number of metal ions adsorbed in the equilibrium phase, q_m the maximum monolayer adsorption (mg/g), and k_l (L /mg) the Langmuir constant related to the adsorption energy. The values for the Langmuir constants k_l and q_m were achieved from slope and intercept of C_e vs. C_e/q_e plot given in Table 2 & Figure 12. In case R^2 is more than 0.99, the surface assimilation of the method follows the Langmuir isotherm. The dimensionless equilibrium parameter R_L is defined to explain the type of isotherm (if $R_L=0$, irreversible; $R_L >1$, unfavorable; $0 < R_L < 1$, favorable; and $R_L = 1$, linear) in the adsorption process obtained from equation(4).³².

$$R_L = \frac{1}{1+K_l C_0} \quad (4)$$

where C_0 is the initial concentration (mg/l). In case the value of R^2 is 0.9965, the Langmuir isotherm fits the adsorption data and since $0 < R_L < 1$, the type of Langmuir isotherm is favorable. The maximum monolayer adsorption (q_m) can be achieved by linear Langmuir isotherm that is estimated to be 48.076 mg/g near the values of experimental maximum adsorption capacity (44.85 mg/g).

Freundlich isotherm

Freundlich equilibrium isotherm model can illustrate the concept of heterogeneous surfaces and assume adsorption on the multilayer surfaces. The parameters of this model (k_f and n) can be calculated from the intercept and slope of $\ln q_e$ vs. $\ln C_e$ diagram, respectively, using equation (5).

$$\ln q_e = \ln K_f + \frac{1}{n} (\ln C_e) \quad (5)$$

where K_f is an adsorption isotherm constant that signifies an approximate adsorption capacity and n is the Freundlich equilibrium constant related to the adsorption intensity. If the value of n ranges from one to ten, the adsorption is assumed favorable. In the case of $n=3.6941$, the adsorption process is favorable. The values of Freundlich constants are given in Table 2 and Figure 12.

Temkin isotherm

Temkin isotherm is elaborated in equations (6) and (7). Through this model, the effect of the indirect interaction of adsorbent on the heat reduction of the adsorption can be clarified³³.

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (6)$$

$$q_e = \frac{RT}{B_T} \ln K_T + \frac{RT}{B_T} \ln C_e \quad (7)$$

B_T (J/mol) constant denotes the heat of the adsorption coverage, and K_T (L/g) is a constant of the binding energy, indicating the significant connection between the adsorbate and adsorbent³³. Moreover, the Temkin isotherm (K_T and B_T) constants can be measured by plotting $\ln q_e$ vs. $\ln C_e$ diagram from the intercept and slope, respectively. The isotherm model plots are given in Figure 12, and all the constant values are summarized in Table 2.

Figure 12. a. the Langmuir, b. the Freundlich, and c. the Temkin isotherms.

((pH of 6, Pb(II) concentration range of (20-130 ppm), contact time (60.0 min), volume of the solution (40 ml), adsorbent dosage of (0.04g), and temperature of (298K))

Isotherm models	Parameters	Adsorption of lead on MIL-53(Al)
Langmuir	Temp	298K
	q_m (mg/g)	48.076
	K_L (l/mg)	0.149
	R^2	0.9965
	R_L	0.049
Freundlich	Temp	298K
	K_f	14.34
	n	3.6941
	R^2	0.9763
Temkin	Temp	298K
	K_T (L/g)	3.9226
	B_T (J/mol)	9.7037
	R^2	0.9712

Table 2. isotherm parameters values of Langmuir, Freundlich, Temkin models for the adsorption of pb(II) on US MIL-53(Al).

Adsorption Kinetic

The kinetic studies were conducted using 0.04 g of UAS MIL-53 (Al) as an adsorbent in the condition characterized by different times (5.0-180.0 min), pH of 6.0, and temperature of 298 K using 20 ppm of the initial concentration to remove lead ion from 40 ml solution. Kinetic models were taken into account to determine the effect of contact time on the adsorption rate and present valuable information about the process mechanism, equilibrium time, and rate control levels. The kinetic models employed to analyze the data and evaluate the adsorption quality included pseudo-first-order and pseudo-second-order as well as intra-particle diffusion kinetic models³⁴. Kinetic results are summarized in Table 3.

Pseudo first-order kinetic reaction

The Pseudo first-order rate is presented in equation (8)³⁵.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

in which q_e (mg/g) is the equilibrium concentration, q_t (mg/g) the concentration at any time, and K_1 (min^{-1}) a pseudo-first-order rate constant. The k_1 and $\ln q_e$ of the pseudo-first-order model can be obtained from the slope and intercept of $\ln (q_e - q_t)$ vs. time plot.

Pseudo-second order kinetic reaction

The pseudo-second-order rate is determined using equation (9)³⁴.

$$\frac{t}{q_t} = \frac{1}{q_e^2 K_2} + \frac{t}{q_e} \quad (9)$$

in which K_2 (g/g.min) is a pseudo-second-order constant. The k_2 and q_e of the pseudo-second-order model can be obtained by plotting the t/q_t vs. time diagram. In this case, the values of $1/q_e$ and $1/k_2 \cdot q_e^2$ can be obtained from the slope and intercept, respectively.

Table 3 presents the kinetic data at C_0 :20 ppm achieved based on their plots. The R^2 values for the pseudo-first-order and pseudo-second-order kinetic models were 0.8547 and 0.9975, respectively. Due to the higher value of the pseudo-second-order R^2 , a better fit for kinetic data was found. Moreover, theoretical values of q_e from the pseudo-first-order rate and pseudo-second-order rate were 10.26 mg/g and 18.51 mg/g, respectively. Furthermore, the experimental q_e was found

at 17.35 mg/g. In the comparison, the consistency between the experimental and theoretical data also confirmed that the pseudo-second-order kinetic model described the adsorption process better, which illustrated that the adsorption rate and the active sites of the adsorbent were comparable.

Intra-Particle Diffusion kinetic reaction

Equation (10) defines the intraparticle diffusion rate to detect the diffusion mechanism and rate control steps of the adsorption process ³⁶.

$$q_t = K_i t^{0.5} + c \quad (10)$$

in which K_i is the intraparticle diffusion rate constant (mg/g.min^{1/2}) and C (mg/g) (Table 3). Intraparticle diffusion predominantly contributes to the rate-limiting step if the correlation diagram of adsorbed ions (q_t) vs. ($t^{0.5}$) gives a straight line through the origin. A dual linear nature is given in Figure 13 based on linear proportion including initial and final stages. The high values of R^2 of the initial stage indicate that the adsorption follows diffusions with the particles or mass transfer. In contrast, another stage involves other adsorption processes that may overcome the challenges of adsorption mechanism.

Figure 13.(a) pseudo first-order kinetic, (b) pseudo second-order kinetic, (c) intraparticle diffusion model.

((pH of 6, Pb(II) concentration (20.0 ppm), contact time range of (5.0-180.0 min), volume of the solution (40 ml), adsorbent dosage (0.04g), and temperature range of (298K))

Models	Parametrs	Data
Pseudo first-order	q_e	10.26
	K_1	0.0356
	R^2	0.8547
Pseudo second-order	q_e	18.518
	K_2	0.00508
	R^2	0.9975
Intraparticle diffusion	C	1.472
	K_i	2.0146
	R^2	0.9933

Table 3. Kinetic- model parameters for the adsorption of Pb(II) on MIL53(Al)

Comparison of adsorption parameter for Pb(II) on different adsorbents

Table 4 compares the lead removal data using various adsorbents. It was found that a significantly small amount of UAS MIL-53(Al) had a moderately better adsorption ability than other samples in a short time. The difference in adsorption rate and capacity of the listed adsorbents lies in different conditions of the adsorption performance, such as temperature, the mass of adsorbent, contact time, the volume of the solution, and difference in surface areas and functional groups. Principally, UAS MIL-53(Al) managed to have a very high adsorption rate of 97.63% in comparison to some other adsorbents at pH 6, due to its hierarchical structure and vaster surface area.

Adsorbent	C _i (ppm)	Contact time (min)	Mass of adsorbent	pH	q (mg/g)	T(K)	Adsorption efficiency	Ref.
UAS MIL-53(Al)	20	60	0.04 g	6	19.526	318	97.63	This study
SAPO-5	60	180	0.12 g	5-6	17.29	-	80.5	34
AIPO-5	60	180	0.12g	5-6	19.9	-	84.5	34
AMCA-MIL53(Al)	400	120	0.075g	5.8	390	318	92	12
Magnetic chrysotile Nanotubes	21.4	-	0.57g/l	5	27.64	298	-	37
Mesoporous silica	828	20	0.05 g	6	84.49	-	51	38
ED-MIL-101(Cr)	50	30	0.02 g	6	81.5	298	-	39

Table 4. Comparison of adsorption parameter for Pb(II) on different adsorbents

Regeneration of adsorbent

The regeneration efficiency of UAS MIL-53(Al) as an adsorbent was evaluated with various elements such as H₂SO₄, H₂SO₄, and HCl. HCL 0.1 M as a strong acid was discovered to be the best desorption of Pb ion to wash the adsorbent with it, rewash it with distilled water, and dry and check its recyclability adsorbent. 0.1 M HCl was used to wash up the Pb(II) for one cycle. The Comparison of adsorption for Pb(II) on Conversion and Ultrasonic synthesis and regeneration of adsorbent in one cycle has shown in Figure14.

Figure 14. Comparison of adsorption parameter for Pb(II) on Conventional and Ultrasonic assisted synthesized and 1cycle regeneration of adsorbent

Conclusion

In the reported study, an efficient and fast method was used to prepare MIL-53(Al), and its impact on the adsorption properties for removing lead ions from aqueous solution was examined. It demonstrates that this Ultrasonic-assisted synthesized MIL-53(Al) can remove lead ions effectively. Compared to conventional synthesis, the sonochemical synthesis managed to shorten the time duration of synthesis from 3 days to 1 day, leading to a faster reaction rate, a hierarchical structure, and a higher external surface area of 1538.6 m²/g and average pore size.

Also, UAS MIL-53(Al) showed a highly effective adsorbent. Compared to other research pieces of literature, the present study proved that increasing the crystallinity and external surface area of MIL-53(Al) lead to significant removal of lead ions due to the synthesis method. The optimal conditions for lead adsorption were achieved using 0.04 mg of adsorbent, 60 min contact time as equilibrium time, an initial concentration (20.0 mg/L), and maximum pH of 6. The higher volume of adsorbent and the longer contact time were found to be factors in increasing the adsorption rate. UAS MIL-53(Al) confirmed the adsorption rate of 97.63% at 315 K temperature, which was shown to increase adsorption with the increasing temperature, meaning that adsorption would be

endothermic. The kinetic data followed a pseudo-second-order rate equation where lead ions were adsorbed onto various sites at different points and had a fast adsorption rate. Data fitted the Langmuir isotherm model, and dynamic and equilibrium surfaces formed perfectly homogeneous surfaces, hence a monolayer coating. In summary, it is expected to use UAS MIL-53(Al) as a promising adsorbent for lead removal from aqueous solutions.

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