Applied Chemistry Today **19(73)** (2024) 131-146

Semnan University

Applied Chemistry Today

Journal homepage: https://chemistry.semnan.ac.ir/

ISSN: 2981-2437

Research Article

Arsenic Removal from Synthetic Wastewater Using UiO-66 and comparing it with Other Adsorbents

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PAPER INFO

Article history:
Received: 08/Jul/2024
Revised: 26/Aug/2024
Accepted: 08/Sep/2024

Keywords:
Adsorption,
Arsenic removal,
Metal organic framework,
Modified zeolite,
UiO-66.

ABSTRACT

The occurrence of arsenic in the surface and groundwater resources threatens human health in time of exposure to people for drinking water, or other applications. In this study, metal organic framework of UiO-66 was synthesized to use for arsenic removal adsorption application. The adsorbent sample was analyzed with XRD & BET before and after removal adsorption. In the XRD analysis of the synthesized UiO-66 adsorbent, strong characteristic peaks indicated that impurities are not seen in the sample crystal structure, and the BET analysis measured its specific area equal to 712.45 m^2/g. The removal of from the synthetic wastewater sample was carried out using UiO-66, natural zeolite treated with acid and base and metal oxide SiO_2 adsorbents. By comparing the sorbents in equal operating conditions, the results showed that UiO-66 and acid-washed zeolite respectively have the highest removal efficiency compared to other nano sorbents. Researchers investigated how different factors affected the removal of arsenic using an adsorbent called UiO-66. They used software of design expert to design experiments that tested the effects of pH, temperature, and the amount of UiO-66 used. The best conditions for arsenic removal were found to be a pH of 9, a temperature of 25°C, and 0.5 grams of UiO-66 per liter. Under these conditions, the maximum arsenic removal was 62.16%, with an adsorption capacity of 10.98 milligrams of arsenic per gram of UiO-66. The researchers also studied adsorption kinetic the arsenic was absorbed and found that the process fit two different models. Finally, they compared UiO-66 to another adsorbent, acid-washed zeolite, and found that UiO-66 removed more arsenic in all cases.

DOI: **https://doi.org/10.22075/chem.2024.34694.2287**

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How to cite this article: miri, Gh., Hematian, S., Daraee M. & Peyvandi, K. (2024). Arsenic Removal from Synthetic Wastewater Using UiO-66 and comparing it with Other Adsorbents. *Applied Chemistry Today*, **19(73)**, 131-146. (in Persian)

1. Introduction

In the last century, pollution caused by urbanization and industrialization has threatened surface and underground water sources [1, 2]. Heavy metals are ecological toxic materials that are widely used in industries and can affect the humans, animals, and plants health [3, 4]. If the wastewater polluted by heavy metals do not treated properly, it make a great threat to human health, thus heavy metal removal from wastewater is of great importance [5]. One of the harmful elements is arsenic, which has four valencies of -3, 0, 3 and 5 [6], among which only As^{5+} (arsenate) and As^{3+} (arsenite) are drinking water pollutants [7]. The concentration of arsenic in contaminated groundwater is 0.5-2.5 ppm and much higher (usually >100 ppm) in industrial wastewaters [8]. Based on World Health Organization (WHO) suggestion, the arsenic ions concentration of drinking water should be less than 10 ppm [3]. Even studies indicate that long-term consumption of drinking water containing arsenic in concentrations of 0.05 ppm and higher can increase the risk of kidney, skin and bladder cancer [9-11]. Hence, arsenic is classified as a first priority toxic substance by the World Health Organization [12]. The results have shown that the adsorption process is an effective process in removing arsenic from drinking water, and this method can easily achieve the amount recommended by the World Health Organization and the American Environmental Protection Agency (0.01 ppm) [13, 14].

Out of all the techniques used to remove arsenic from water, like coagulation and filtration, researchers are especially interested in adsorption because it's efficient, affordable, and easy to use [6]. Figure 1 illustrates various methods for removing heavy metals from polluted water. However, traditional materials used for adsorption often have limited capacity [15]. For this reason, it is very important to choose the right adsorbent. Recently, a new type of material called metal-organic frameworks (MOFs) has shown promise as an effective adsorbent for removing harmful heavy metals from water [16].

MOFs have attracted attention due to their porosity and high surface area, chemically tunable nature, reusability, structural features and performance, and are being evaluated for use in a variety of adsorption applications [17]. However, many MOFs are unstable in the presence of water, which severely limits their usefulness, but the UiO-66 sample is a common form of Zr-MOFs that shows good adsorption performance with good thermal stability (<500°C) and water resistance [18-20]. UiO-66 is a special type of material called a Metal-Organic Framework (MOF). Its core building block is a cage-like structure made of zirconium and oxygen atoms ($Zr_6O_4(OH)_4$ cluster). An important property of UiO-66 is its exceptional stability. The strong chemical bonds between zirconium and oxygen make it resistant to acidic and alkaline environments. This stability is a key reason why UiO-66 is considered promising for water purification applications [21].

Several factors influence how well adsorption removes pollutants from water. These factors include the type of pollutant and its concentration, the properties of the material used for adsorption (the adsorbent), and the conditions during the process like pH, temperature, and effect of contact time and effect of initial concentration with the adsorbent. Researchers have improved the effectiveness of UiO-66, a metal-organic framework (MOF), for removing heavy metals from water. For example, Fu et al. (2019) modified UiO-66 to remove lead (Pb) more selectively, achieving a capacity of 189.9 milligrams of lead per gram of adsorbent at a pH of 4 [22]. Other studies have shown success in using UiO-66 to remove other heavy metals like cadmium, chromium, mercury.

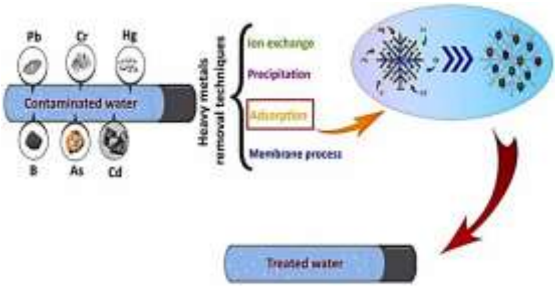


Fig. 1. Methods of removing heavy metals from polluted water [16].

Such as Farhad et al. (2021) [23] were tested to enhance the treatment of Pb (II) using two amine ligands possessed by ethylenediamine (EDA) as a ligand for UiO-66 grafting, they achieved an adsorption capacity of 243.90 mg/g for Pb (II) and also, Saleem et al. (2016) [24] had modified the UiO-66 adsorbent for heavy metal treatment and improved the Cd^{2+} ,Cr^{3+} ,Pb^{2+} and Hg^{2+} ions adsorption removal efficiency, respectively to adsorption capacities of 49, 117, 232 and 769 mg/g. Additionally, researchers have explored alternative MOFs for arsenic removal. Zhang et al. (2023) demonstrated a cerium-based MOF that can rapidly remove almost all arsenic from water within 10 minutes [25]. Ren et al. (2023) [26] used a composite of magnetic core @ Shell Fe_3O_4 @ polypyrrole @ sodium dodecyl sulfate for selective removal of five dyestuffs and heavy metal ions from complex wastewater. They reached a removal efficiency above 90% after five desorption–adsorption cycles and confirmed that their adsorbent composite is a promising candidate for dyestuffs and heavy metal removal. In a study examined the ability of olive leaf ash to remove copper, lead, and chromium ions from water. Factors like pH, temperature, contact time, and adsorbent dosage were tested to determine the best conditions for adsorption. The adsorption data was analyzed using Langmuir, Freundlich, and Tempkin models, with the Langmuir model providing the best fit. Kinetic studies using pseudo-first order, pseudo-second order, and intraparticle diffusion models indicated that the pseudo-second order model accurately describes the adsorption process. Thermodynamic analysis showed that the process is both endothermic (requires heat) and spontaneous (occurs naturally) [27]. This article explores the use of polypyrrole and its nanocomposites as materials for removing copper ions from water. Polypyrrole was synthesized using a chemical oxidation process with iron chloride as the oxidizing agent. The ability of polypyrrole, polypyrrole/titanium dioxide, and polypyrrole/titanium dioxide/sodium dodecyl sulfate nanocomposites to remove copper ions was investigated. Batch experiments were conducted to determine the optimal conditions for copper ion removal, including pH, ion dosage, and contact time. The results showed that the best conditions were a pH of 3, an ion dosage of 50 mg/L, and an equilibrium time of 30 minutes. The Freundlich adsorption isotherm model was found to accurately describe the equilibrium adsorption behaviour [28]. Many toxic heavy metals, such as lead, cadmium, mercury, copper, nickel, zinc, and chromium, are released into the environment as industrial waste, contaminating soil and water. Industrial wastewater containing these metals can pollute nearby water bodies. Heavy metals tend to accumulate in organisms, leading to various health problems. They are also common groundwater contaminants at industrial and military sites. Several methods exist for removing dissolved heavy metals from water, including ion exchange, precipitation, extraction, ultrafiltration, reverse osmosis, and solid-phase extraction. Recently, there has been a focus on using low-cost materials as potential adsorbents for heavy metal removal [29]. In other study investigates the ability of low-cost orange tree leaves to remove heavy metal ions (cobalt, cadmium, and zinc) from water. The adsorption process was analyzed using Freundlich, Langmuir, and Temkin isotherms. The kinetic data was best described by the pseudo-second order model, and thermodynamic studies showed that the process is spontaneous and requires heat. The adsorption of all three metals increased with higher pH but decreased with higher temperature and metal ion concentration. The results suggest that using orange tree leaves is a simple, inexpensive, and effective method for removing heavy metal ions from water and wastewater [30].

In this study, we compared the effectiveness of different materials for removing arsenic from synthetic wastewater. We tested UiO-66, acid and base-treated zeolite, and silicon dioxide nanoparticles (SiO_2). We identified the best performing material and evaluated its effectiveness under various conditions. Finally, we compared the performance of the two best materials under the five most favorable conditions identified in our study.

2. Experimental

2.1. Materials and Physical Measurements

This study utilized several chemicals for the synthesis of UiO-66. Zirconium chloride ($ZrCl_4$), terephthalic acid (H_2BDC), N,N-dimethylformamide (DMF), and methanol (CH_3OH) were all obtained from Merck Chemical Company. Additionally, arsenic oxide (As_2O_3) was sourced from Sigma Aldrich Company. Crystallographical structure, composition and crystallinity of the nanocomposites were determined by X-ray diffraction (XRD) patterns, acquired by Bruker AXS-D8 Advance X-ray diffractometer model for low (0.5–10 °) and high-angle X-ray diffractions (5–80 °) which was equipped with a Cu-Kα radiation source. Characterization of pore sizes and adsorption capacity of the materials is accomplished using physical sorption measurement. Equilibrium adsorption isotherms of N_2 are measured using standard volumetric techniques (ASAP 2010, Micromeritics). The specific surface areas are calculated using the BET approach (BrunauerEmmett-Teller).

2.2. Synthesis of UiO-66

For the synthesis of UiO-66, 1.8 g of 98% zirconium tetrachloride and 75 ml of 99% N,N^1 -dimethylformamide (DMF), and at the same time 1.8 g of 99% terephthalic acid and 150 ml DMF was placed in separate beakers on a stirrer for 30 minutes at a speed of 500 rpm. Then, the two compounds were mixed together and placed on the stirrer at 500 rpm for 15 minutes, to combine $ZrCl_4$ and BDC in DMF under stirring condition. Then the UiO-66 solution was transferred to Teflon-coated stainless-steel autoclaves and dried in oven at 120 ℃ for 24 hours. The dried UiO-66 powders were washed three times with methanol and three times with DMF using 10,000 rpm centrifuge at 5 ℃ for 3 min to separate solid from the washing solvent, and finally dried at 120 ℃ for 24 hours in an oven to be ready for use as a suggested adsorbent. Figure 2 (a) & (b) shows the synthesized UiO-66 after drying and its structure respectively [18]. According to Figure 2b, the metal organic frameworks are crystalline porous materials composed of three-dimensional layers, which are composed of an organic connecting part and a part containing inorganic metal nodes (or metal-containing clusters). Therefore, these adsorbents are also called organic-mineral.

2.3. Modification of natural zeolite

The zeolite used in this experiment was the natural clinoptilolite zeolite. After the meshing process, zeolite with mesh of 35 (500 micrometer) was used for zeolite adsorption application. In order to zeolite modification, it was placed in double-distilled water for 24 hours to wash and remove the impurities.

For acid washing, the zeolite was washed with nitric acid 0.5 M for 2 hours on a stirrer at a speed of 500 rpm, and then it was placed in double-distilled water for 24 hours. Then treated with acid to reach neutral pH. After the zeolite was placed in the environment for 12 hours and dried, it was placed in an oven at a temperature of 100°C for 12 hours to remove its moisture. Figure 3 shows the final prepared sample. This sample will be used in the next steps to investigate the adsorption process.

Fig.2. Synthesized UiO-66 and its structure [27].

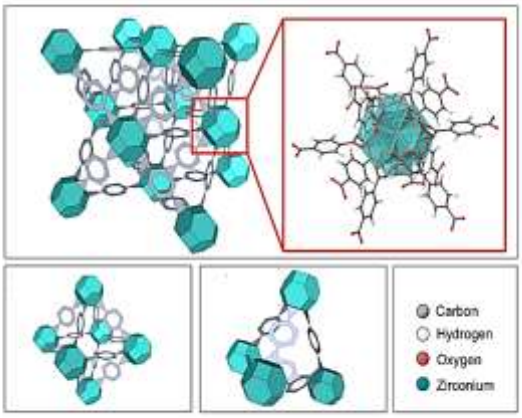
Fig.3. Acid-washed zeolite after drying.

2.4. Preparation of arsenic wastewater

Arsenic trioxide and sodium hydroxide were used to prepare arsenic wastewater samples. To make a 1000 ppm stock solution, 1.320 g of solid arsenic was dissolved with 4 g of sodium hydroxide as an arsenic dissolving agent in double-distilled water and brought to a volume of 1000 ml in a volumetric balloon and steered at room temperature (25 ± 1 ℃).

2.5. Adsorption Experiments

Researchers investigated how well UiO-66 adsorbs arsenic. They prepared a solution with a consistent arsenic concentration of 50 ppm by diluting a stock solution with clean water. A software program (Design-Expert) was used to design experiments that tested the effects of three main factors on the adsorption process: pH, temperature, and the amount of UiO-66 used (see Table 1 for details).



The experiments were conducted in glass beakers containing 100 ml of the wastewater sample with the constant arsenic concentration. The pH of the solution was adjusted to 5, 7, or 9. The temperature was set to 25, 45, or 65°C. Different amounts of UiO-66 adsorbent (0.1 g, 0.3 g, or 0.5 g) were added to each beaker.

Table 1. The variable parameters for experimental design run and results of arsenic removal obtained from the adsorption in 16 experiments.

Run	Temp (°C)	pH	UiO-66 (gr)	% of removal
1	45	7	0.3	27.08
2	45	5	0.3	25.52
3	25	9	0.1	30.16
4	45	9	0.3	29.14
5	25	5	0.5	51.86
6	65	9	0.5	58.6
7	45	7	0.5	57.84
8	45	7	0.1	21.96
9	65	9	0.1	27.66
10	25	7	0.3	30.28
11	45	7	0.3	27.42
12	25	5	0.1	24.42
13	65	5	0.5	46.92
14	65	5	0.1	19.36
15	65	7	0.3	28.4
16	25	9	0.5	62.16

Each beaker was placed on a stirrer set to 800 rpm for 90 minutes to ensure good contact between the arsenic and the UiO-66. The solution was then filtered using Whatman 41 filter paper. An instrument called an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) was used to measure the amount of arsenic remaining in the filtered solution.

Equation 1 (shown here) is used to calculate the percentage of arsenic removed from the wastewater based on the initial concentration and the concentration remaining after treatment.

$$R = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

2.6. Kinetics and isotherms

2.6.1. Kinetic models

In order to better understanding of the adsorption mechanism, kinetic model evaluation was carried out. Thus, the time depending adsorption data were fitted on the linear forms of pseudo-second order and Elovich kinetic models.

Equations 2&3 represent the linear forms of pseudo-second order and Elovich kinetic models respectively [31, 33].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (2)$$

Where; q_t (mg/g) represents the arsenic time dependent adsorbent capacity, q_e (mg/g) is the equilibrium adsorbent capacity and K_2 (g/mg.min) is the pseudo-second order rate constant.

The Elovich kinetic model is:

$$q_t = \frac{1}{\beta} \ln \alpha\beta + \frac{1}{\beta} \ln t \qquad (3)$$

With the desorption constant of β (g/mg), and the initial adsorption rate of α (mg.min/g).

2.6.2. Adsorption Isotherms

The equilibrium isotherm shows how the molecules of the adsorbed substance are divided between the liquid and solid phases after reaching the equilibrium condition of the adsorption process. Equilibrium data between the solid and liquid phases can describe the dynamic adsorption of contaminant in the mixture of wastewater and adsorbent. Through the Isotherms of adsorption and their theories, it is possible to realize the equilibrium capacity of adsorbent, type of adsorption, theoretical maximum capacity, etc. [34].

Langmuir Adsorption Model. The Langmuir isotherm describes a specific type of adsorption where molecules form a single layer on a perfectly uniform surface. The model assumes there's no interaction between the adsorbed molecules. The process reaches equilibrium when this single layer is completely filled. Equation 4 expresses the Langmuir isotherm in a linear form, which is often used for data analysis [35].

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{b q_m C_e} \qquad (4)$$

In this regard, the term q_e (milligrams of pollutant adsorbed per gram of adsorbent) represents the amount of arsenic adsorbed onto the UiO-66 at equilibrium. Ce (milligrams of arsenic per liter) refers to the concentration of arsenic remaining in the solution after reaching equilibrium. The value of q_m (milligrams of arsenic per gram of adsorbent) in the Langmuir equation reflects the theoretical maximum adsorption capacity of the UiO-66. This essentially represents the highest amount of arsenic the UiO-66 could potentially adsorb under ideal conditions [35].

Separation factor or equilibrium parameter is an important dimensionless parameter obtained from the equation 5. According to the value of the separation factor, the process is divided into four categories: unfavorable, linear, favorable and irreversible [36].

$$R_L = \frac{1}{1 + b C_0} \qquad (5)$$

Freundlich Adsorption Model. Unlike the Langmuir model, the Freundlich model represents multilayer adsorption on a surface that is heterogeneous in terms of energy, and in addition, the adsorbed molecules interact [35] . Equation 6 represents the linear form of Freundlich Isotherm.

$$\mathrm{Ln}\, q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (6)$$

This sentence explains how two constants, K_F and n, are determined from the Freundlich isotherm equation (which is not explicitly mentioned here but describes how a pollutant interacts with an adsorbent). These constants are important for understanding how well a material adsorbs a pollutant. In this regard, K_F is constant that is related to the adsorption capacity of the material. A higher K_F value indicates that the material can hold more of the pollutant. Also, n is constant that reflects the adsorbent strength. A value of n between 1 and 2 generally suggests a favorable adsorption process, where the pollutant is more easily adsorbed at lower concentrations. These constants (K_F and n) are calculated by fitting a straight line to a graph where the y-axis is the natural logarithm of the amount of pollutant adsorbed ($\ln(q_e)$) and the x-axis is the natural logarithm of the equilibrium concentration of the pollutant ($\ln(C_e)$). The slope of this fitted line corresponds to the value of n, and the K_F value is related to the position of the line relative to the origin.

2.7. Response Surface Methodology (RSM)

In this section, we explain how designed our experiments to understand how different factors affect arsenic removal using UiO-66. We use advanced statistical method as a technique called Response Surface Methodology (RSM) to analyze the data. RSM is a powerful statistical tool that helps identify how individual factors and their interactions influence a final outcome. Then, we investigated **v**isualizing the effects**.** RSM is used a graphical representation called a "response surface" to show these effects. This allows us to see how changing multiple factors simultaneously affects the final result.

Then, we do experimental design to do a specific design with three levels for each variable (-1, 0, and 1). These levels represent different settings for the factors being tested (like pH, temperature, and adsorbent amount). Then, we carried out mathematical model**.** We developed a mathematical model based on a second-order polynomial equation to describe how these variables affect arsenic removal. Finally, we evaluating effectiveness is done as an analysis of variance (ANOVA) that be used to assess how statistically significant the impact of each variable and their interactions are on the amount of arsenic removed. This would help identify which factors have the strongest influence on the process.

3. Results and discussion

In the first stage, after preparing a synthetic solution containing a constant concentration of 250 ppm arsenic at pH=13; the adsorption process carried out in constant temperature (25 ± 1 °C), for a period of 30 minutes. The results obtained from ICP-OES analysis showed that UiO-66 and acid-washed zeolite have the highest arsenic removal efficiency compared to other adsorbents (Figure 4).

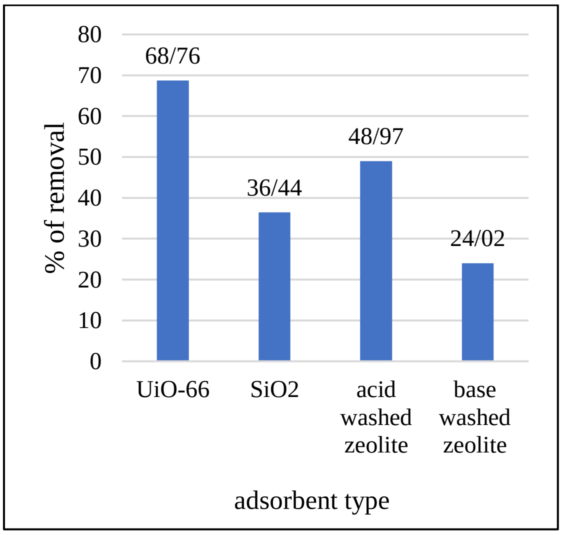


Fig.4. Comparison of different adsorbents in terms of removal percentage.

3.1. Characterization techniques

XRD Analysis. The X-ray diffraction pattern of the synthesized UiO-66 material is shown in Figure 5. Strong characteristic peaks are observed with the appearance of three distinct peaks at 2θ angles of 7.4, 8.5 and 25.7 degrees and weaker peaks at 2θ angles of 14.8, 17.1 and 30.7 degrees. In general, these peaks are consistent with the XRD patterns previously reported for UiO-66, and the characteristic data show that no impurities can be seen in its crystal structure and the synthesis of the UiO-66 framework has been successfully completed [18].

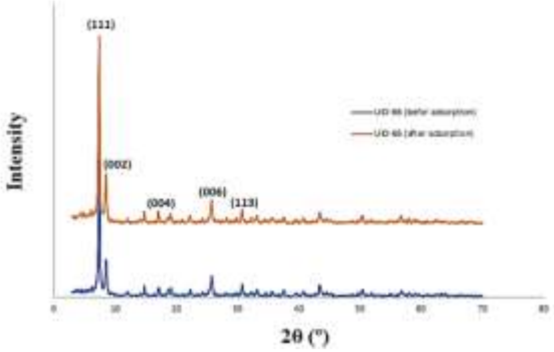
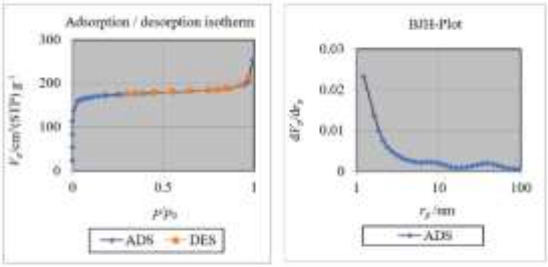


Fig. 5. X-ray diffraction pattern of UiO-66 synthesized in this research.

The consistency of patterns before and after adsorption indicates the ability of adsorbent to be reused.

The Brunauer-Emmett-Teller (BET) analysis. Nitrogen adsorption-desorption isotherm for the synthesized UiO-66 is shown in Figure 6(a). Based on IUPAC classification, the obtained curve is of type (I). This type of adsorption shows that at low pressures, the adsorbent surface is largely unoccupied, and adsorption occurs rapidly. Then, as the pressure increases, the surface becomes progressively covered until a saturated monolayer is formed. This feature is characteristic of microporous particles. However, there is a hysteresis between the adsorption and desorption curves, which indicates the nature of microporous particles in combination with some mesoporous and macroporous particles [37, 38]. Figure 6(b) shows the diameter distribution of synthetic adsorbent pores, which shows that most of the pores have a diameter below 10 nm, but a small percentage of them have a diameter bigger than 10 nm, which indicates the presence of meso and macro pores.



(a) (b)

Fig. 6. The results of BET analysis (a) adsorption-desorption curves, (b) distribution curve of pore diameter.

The surface characteristics of the sample are given in Table 2.

Table 2. Specific surface area, diameter and volume of UiO-66 adsorbent pore.

Total pore volume (cm^3/g)	**Average pore diameter (nm)**	**Specific surface area (m^2/g)**
0.38	2.2	712.45

3.2. Mathematical Model and analysis of variance (ANOVA)

The experiments suggested by the experimental design were performed and the response values of each run were recorded. The results of SRM regression resulted in mathematical relationship of equation 9.

$$R=28.06-0.6060\times A+3.96\times B+15.38\times C-0.7425\times AB+1.12\times AC+0.9925\times BC+1.88\times A^2-1.13\times B^2+11.44\times C^2 \qquad (9)$$

Where:

A: temperature (℃)

B: pH

C: mass of UiO-66 (g)

This good agreement is further supported by the strong correlation between two statistical measures, R-squared (R^2) and adjusted R-squared (adjusted R^2). High values for both suggest the model effectively captures the relationship between the variables and the outcome (arsenic removal). However, it's important to note that the model's predictions are only reliable within a specific range of the experimental conditions tested (the operative parameters). It might not be accurate outside this range.

Table 3 summarizes the results of a statistical analysis (analysis of variance) to determine which factors and interactions significantly influence arsenic removal. P-value is used as an indicator here. Factors with a p-value less than 0.05 are considered statistically significant, meaning they have a substantial impact on the outcome. Table 4 presents the detailed statistical analysis of the proposed model for arsenic removal adsorption. It likely includes information about the specific coefficients and terms used in the second-order polynomial equation mentioned earlier (Figure 7).

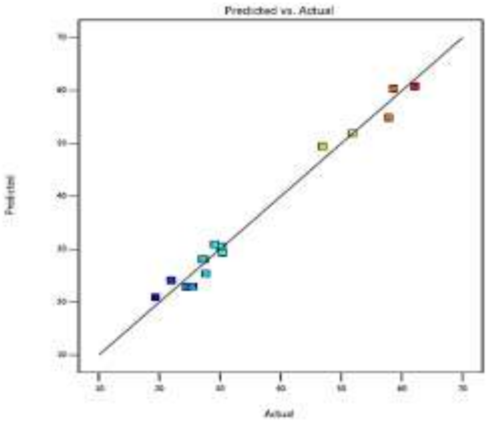


Fig.7. Actual values of arsenic removal results vs. predicted ones.

3.3. The effects of parameters on arsenic removal

The behavior of arsenic adsorption in the temperature range of 25-65 ℃ was investigated. Figure 8 shows the interaction of temperature and pH parameters on the efficiency of arsenic adsorption by the adsorbent. It can be seen that at a temperature of 25 ℃ and alkaline pH (pH=9), adsorption has been more efficient than other areas. Reducing the temperature favors the surface adsorption process. This issue was expected due to the exothermic nature of the surface adsorption process [39, 40]. Figure 8 shows the effect of various temperature for removal.

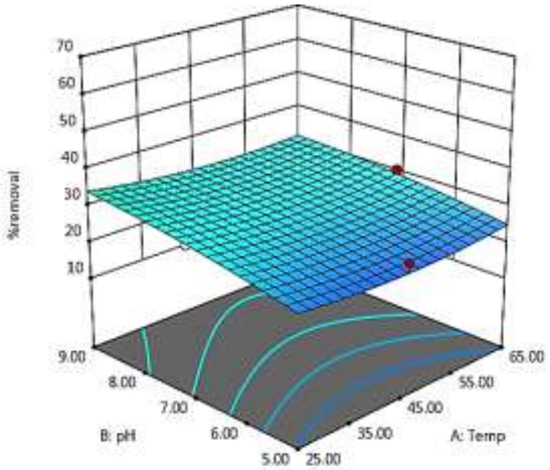


Fig. 8. Response surface plot of temperature and pH in the arsenic removal adsorption.

Figure 9 shows the parameters interaction of temperature and mass of Ui-66 on the efficiency of arsenic adsorption by the adsorbent. It can be seen that at a temperature of 25 ℃ and biggest amount of UiO-66, adsorption has been more efficient than other areas. Increasing the amount of adsorbent provides more adsorption sites for arsenic and consequently increases the adsorption performance in arsenic removal from wastewater.

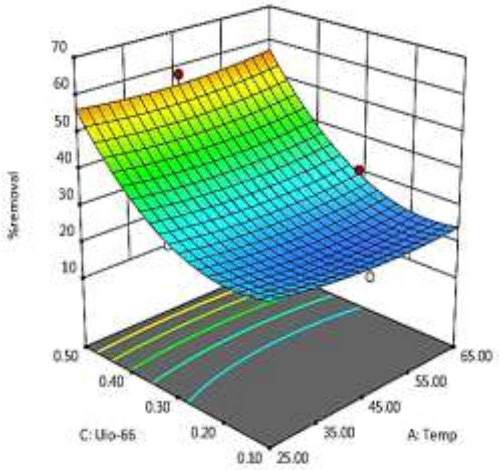


Fig. 9. Response surface plot of temperature and mass of Ui-66 in the arsenic removal adsorption.

Figure 10 shows the parameters interaction of pH and mass of UiO-66 on the efficiency of arsenic adsorption by the adsorbent.

Table 3. Statistical analysis data of proposed model through the experimental design describing arsenic removal adsorption.

Source	Sum of squares	df	Mean square	F-value	P-value	
Model	3089.70	9	343.30	55.09	< 0.0001	significant
A	25.41	1	25.41	4.08	0.0900	
B	157.13	1	157.13	25.21	0.0024	
C	2366.06	1	2366.06	379.65	< 0.0001	
AB	1.94	1	1.94	0.3114	0.5970	
AC	0.1105	1	0.1105	0.0177	0.8984	
BC	7.88	1	7.88	1.26	0.3038	
A^2	9.30	1	9.30	1.49	0.2676	
B^2	3.37	1	3.37	0.5415	0.4896	
C^2	344.95	1	344.95	55.35	0.0003	
Residual	37.39	6	6.23			
Lack of fit	37.34	5	7.47	129.19	0.0667	Not-significant
Pure Error	0.0578	1	0.0578			
Correlation- total	3127.09	15				

The results show the adsorbent amount, alkaline pH and the temperature have biggest impact on arsenic removal respectively. The impact of alkaline pH on the arsenic adsorption improvement can be attributed to the pH point of surface zero charge. Below the pH of zero charge, adsorbent has a positive surface charge that establishes an electrostatic force of repulsion with positively charged arsenic.

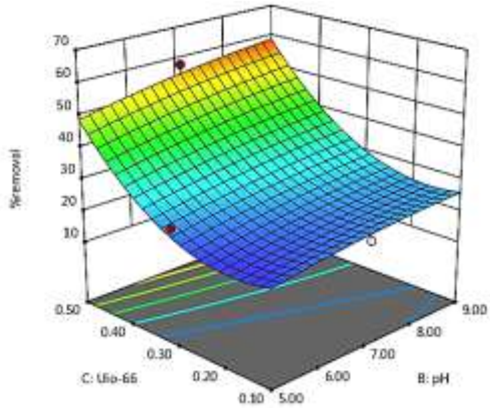


Fig. 10. Response surface plot of pH and mass of UiO-66 in the arsenic removal adsorption.

By increasing the pH of the solution to alkaline values, the adsorbent surface charge becomes negative, and UiO-66 can attract the positively charged arsenic and capture a larger amount of pollutant.

3.4. Optimum operational conditions

Design Expert can estimate the optimal values of the parameters evaluated in adsorption study to achieve maximum efficiency of arsenic removal. Table 4 shows the optimum operational conditions of this study.

Table 4. Optimum conditions of adsorption arsenic removal.

Temperature (℃)	pH	UiO-66 (g)	% of removal
25	9	0.5	62.16

3.5. Adsorption kinetics

In this section, the kinetics parameters of the adsorption process at 25 °C, pH=9, adsorbent dose equal to 0.5 g and effluent concentration of 50 ppm were obtained (Table 5 and Figure 11). Our data fits a pseudo-second-order kinetic model, it suggests that the rate of the reaction is proportional to the square of the concentration of one of the reactants.

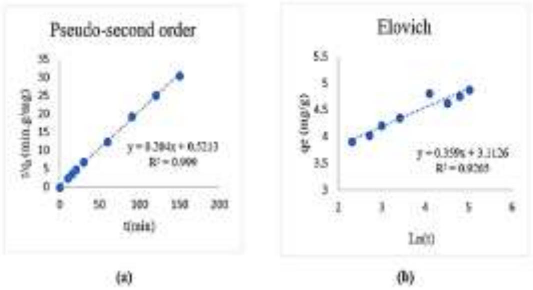


Fig .11. Matching the data of arsenic absorption process by UiO-66 with the kinetic equation. (a) Pseudo-second order, (b) Elovich

This model describes heterogeneous reactions, where the rate is influenced by factors like surface area and adsorption.

3.6. Adsorption isotherms

Equilibrium isotherms of arsenic adsorption process by UiO-66 were investigated at the optimum conditions of temperature, pH and adsorbent dosage equal to 25 °C, 9 and 0.5 g, respectively. Figure 12 shows the fitting of experimental data on the linear forms of Langmuir, Freundlich, equilibrium isotherms in the process of arsenic adsorption by UiO-66 adsorbent.

Table 6 shows the parameters obtained from linear data fitting of Langmuir, Freundlich equilibrium isotherms. There are some reasons for fitting of experimental data on the linear forms of Langmuir and, Freundlich. The first is surface inhomogeneity. The surface of the adsorbent may not be completely homogeneous and may have active sites with different energies. The second is changes in the adsorbent structure.

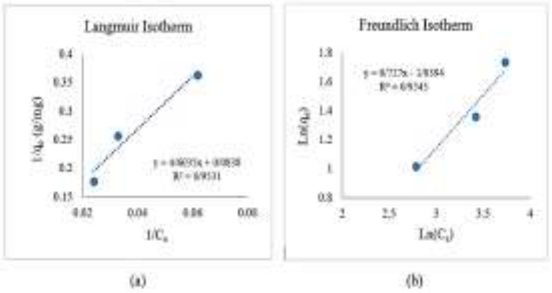


Fig.12. Matching the data of arsenic adsorption isotherms using UiO-66. (a) Langmuir, (b) Freundlich,

During adsorption, the adsorbent structure may change and this change causes the adsorption behavior to change from Langmuir to Freundlich model.

Finally, interference between adsorbed molecules. As the concentration of adsorbed substance increases, the interference between adsorbed molecules increases and this interference causes the behavior of absorption to change from Langmuir to Freundlich model.

3.7. Comparison of UiO-66 & acid-washed zeolite

Table 7 lists five best runs and their conditions resulted from experimental design. Figure 13 also compares the five best runs for acid-washed zeolite and UiO-66 adsorbents. As can be seen, in all operating conditions, UiO-66 has shown better performance than acid-washed zeolite.

As can be seen, in 5 runs the percentage of arsenic removal by UiO-66 is higher than the results related to acid-washed zeolite. The synthesized metal-organic framework provides a higher efficiency comparing to zeolite and this shows the superiority of UiO-66 adsorbent over zeolite modified by acid washed process.

Table 5. Constants of Pseudo-second order, and Elovich kinetic models for arsenic absorption by UiO-66

Temperature (℃)	Pseudo-second order			Elovich		
	R^2	q_e (mg/g)	k_2	R^2	β(g/mg)	α (mg.min/g)
25	0.999	4.9019	0.07983	0.9265	2.785515	2091.762

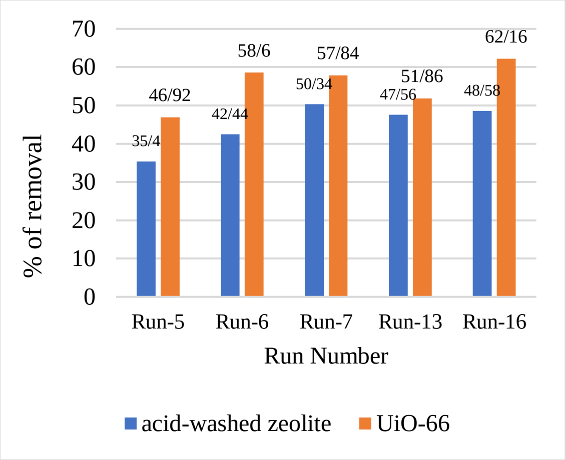


Fig.13. Comparing the best runs for acid-washed zeolite and UiO-66 adsorbents.

4. Conclusion

Since adsorption is a cost-effective method for removing arsenic from water, researchers are constantly searching for efficient adsorbent materials. This study focused on comparing the effectiveness of several potential adsorbents for arsenic removal. The synthesized UiO-66 material was investigated alongside silicon dioxide nanoparticles (SiO_2) and both acid-washed and base-washed zeolite. The aim was to identify the best candidate for removing arsenic from water resources. Among them, UiO-66, acid-washed zeolite, SiO_2 nanoparticles and base-washed zeolite showed highest and second highest performance respectively.

UiO-66 was selected in order to its removal capacity of arsenic from wastewater be evaluated under variation of effective parameters including temperature, pH and dosage of adsorbent.

Results illustrated that temperature has a reverse impact on the adsorption due to the exothermic nature of adsorption process, in alkaline pH, surface charge of UiO-66 becomes negative and its negativity becomes stronger in higher pHs.

Table 7. Repeating the best runs with acid-washed zeolite adsorbent

Run	Temp (°C)	pH	adsorbent (gr)	% of removal	
				UiO-66	Acid-washed zeolite
5	25	5	0.5	46.92	35.44
6	65	9	0.5	58.6	42.44
7	45	7	0.5	57.84	50.34
13	65	5	0.5	51.86	47.56
16	25	9	0.5	62.16	48.58

Consequently, adsorption at higher pHs due to attractive electrostatic forces between adsorbent and pollutant becomes favorable. Also increasing the dosage of adsorbent provides more adsorption sites for constant amounts and favors the adsorption performance. Therefore, the optimum conditions (the maximum % of removal equal to 62.16%) for temperature, pH and adsorbent dosage were 25 ℃, 9 and 0.5 g respectively. Also, the maximum adsorption capacity of 13.83 mg/g was obtained.

Kinetic and isotherm studies revealed that the adsorption process follows pseudo-second order (R^2=0.999) and Elovich (R^2=0.9265) kinetic models and Longmuir (R^2=0.9531) and Freundlich (R^2=0.9545) adsorption isotherms, respectively. The adsorption arsenic removal of UiO-66 and acid-washed zeolite in five best conditions of experiment-

Table 6. Constants of Freundlich, and Langmuir isotherm models for arsenic absorption by UiO-66

Temperature (℃)	Freundlich			Langmuir			
	R^2	K_F (mg/g)	n	R_L	R^2	q_m (mg/g)	b (L/mg)
25	0.954	1.571	1.375	0.5235	0.953	11.933	0.0182

-al design suggested runs revealed that in all conditions UiO-66 has a better adsorption behavior comparing to acid-washed zeolite.

Declarations:

Ethical Statements:

The authors confirm that no part of this research includes human or animal testing. Ethical considerations have been made to protect the environment.

Competing interests

The authors declare no competing interests.

Funding:

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

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