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Aqueous sequestration of Lead Ions by Zn-based metal-organic framework (MOF5): Equilibrium, kinetics, and pH studies

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ABSTRACT

Lead is a potentially toxic metal which easily contaminates water forms due to its ubiquitous applications. The demonstration of viable techniques to remove Lead ions from water is one of the most researched topics. In this study, the highly reported surface and pore advantages exhibited by metal-organic frameworks is exploited for the trapping of aqueous Lead. The Zinc-based MOF5 was synthesized for adsorption tests involving the sequestration of Lead ions. Tests were conducted to determine the effects of concentration, contact time and pH in the uptake of Lead ions from solution. The extent of adsorption was evaluated as percentage uptake of Lead and Lead uptake capacity of MOF5. The results showed that while the percentage uptake and Lead uptake capacity of MOF5 depended on the concentration and pH of solution, contact time had only minimal effects. Five adsorption isotherms were applied to evaluate the adsorption data including Dubinin-Radushkevich, Freundlich, Langmuir, Elovich and Jovanovich. However, the R^2 values gave the Elovich isotherm ($R^2 = 0.8029$) as the best fitting model, implying the dominance of multilayer interaction between MOF5 and Lead ions. The pseudo-second-order kinetics and the Webber-Morris intraparticle diffusion were also applied to evaluate the kinetics of the process. The pseudo-second-order kinetic plots were observed to provide the better fit to the kinetics, ahead of the Webber-Morris intraparticle diffusion, depicting the dominance of chemisorption. The high percentage (> 90 %) of Lead ions taken up, and the high capacity of MOF5 for the ions, as observed across all three types of adsorption tests performed, demonstrates that MOF5 (> 45 mg/g) could represent an efficient adsorbent for the targeted separation of Lead ions during water treatment.

Keywords: metal-organic framework, Lead ion uptake, Adsorption Isotherm, Adsorption kinetic models

1. INTRODUCTION

Lead contamination of aqueous media is a common occurrence and major cause for toxicological concerns. Thus, has led to many solution-oriented researches and development of diverse techniques for the removal of lead from water (Agbozu et al., 2008). Lead has a wide spectrum of application, hence it easily comes into contact with water forms, and also leaches through easily due to its appreciably high aqueous solubility (WHO, 2022; Alorabi et al., 2020). Its continued contamination of water, and its growing distribution in areas such as groundwater aquifers, surface water and drinking water, have become the cause for concern (Ukachuku & Abasi, 2021).

Lead is non-biodegradable, hence exhibit a high potential to bioconcentrate and bio-magnify in life's forms (Ukachuku & Abasi, 2021). Excerpts from reports on Lead toxicity has it that Lead affects almost every human organ-systems. Lead causes nephrotoxicity, neurotoxicity, reproductive toxicity, and cardiotoxicity in humans (Wani et al., 2015), while also being linked with growth impairments in plants (Pourrut et al., 2011).

To tackle the problem of lead contamination of surface and ground water, many research efforts have focused on the adsorption techniques where many different kinds of adsorbents have been studied, including: gamma irradiated minerals (Cruz-Olivares et al., 2016), cellulosic materials (Agbozu et al., 2008; Ukachuku & Abasi, 2021), activated carbons (Shi et al., 2018; Alghamdi et al., 2019; Mekonen, 2022), algal materials (Hammud et al., 2014) and so on.

This study contributes to the global scientific efforts to curb lead contamination of water forms by the utilization of the highly porous metal-organic framework for pore trapping and immobilization of the ions. Metal-organic frameworks (MOF) are porous crystalline materials composed of metal clusters bridged by organic ligands. They were first reported in the early 1990s (Yaghi et al., 2019).

The Zn-based metal-organic framework, MOF5, was one of the earliest MOFs, and was synthesized for hydrogen gas storage (Yaghi et al., 2019; Kaye et al., 2007). MOF5 (also called Isorecticular MOF-1 or IRMOF-1) was synthesized by high temperature refluxing of a mixture of zinc nitrate tetrahydrate and terephthalic acid linker in N, N-Dimethyl formamide solvent, yielding a three-dimensional material with cubic topology, high surface area and high pore volume (Kaye et al., 2007).

Here, we adopted the reported solvothermal procedure to reproduce MOF5 for application in Lead ion removal from water.

The material being known for its sophisticated pore properties, showing exceptional surface area and pore volume, as has been reported in several studies, could serve as a potential trap to immobilize lead ions and keep them trapped within its pores. In this study, we prioritize the equilibrium, kinetics, and pH studies of the sorption process.

In the equilibrium and kinetic studies, we simply applied adsorption regression models for both equilibrium adsorption and kinetics and draw conclusions on the extent of sorption and sorption mechanism based on the percentage of data that fits the applied model. In the pH studies, we simply determined the pH of maximum sorption.

2. MATERIALS AND METHOD

List of reagents: The Zn metal constituent of MOF5 was supplied by Zinc nitrate hexahydrate purchased from Aladdin Biological Technology Co, LTD, Shanghai, China. The organic linker, 1,4-benzene dicarboxylic acid (terephthalic acid) was purchased from Merck KGaA, Darmstadt, Germany. Others were N, N-dimethyl formamide (also from Merck KGaA, Darmstadt, Germany), methanol (Guangdong Guanghua Sci-tech, China) and lead nitrate (Fisher Scientific Company, U.S) used in the preparation of model lead contaminated waters. All reagents were of analytical grade and were used without further purification.

Synthesis of MOF5: The solvothermal method of Dikio & Farah, 2013, was applied. 4.46 g of zinc nitrate hexahydrate and 2.49 g of were added to 60 ml of N, N-dimethyl formamide in a round-bottom flask. Resulting mixture was heated under reflux to a temperature of 140 °C and maintained for 10 hours. The resulting white crystalline material was washed in methanol to expunge trapped guest molecules. Thereafter, it was oven dried and stored in sample bottles.

Preparation of model solutions: A stock solution of 500 mg/L was prepared by dissolving 800 mg of Lead nitrate in 1 L of distilled water. Five working concentrations, 10, 20, 30, 40, and 50 mg/L were prepared through serial dilution. Ten other solutions (20 mg/L each) were prepared for contact time and pH studies respectively.

Lead ion sequestration tests: Batch sorption techniques were utilized to determine the capacity of MOF5 (applied in its pristine condition without any further modification) to take up Lead ions from model solutions. The extent of Lead ion uptake was studied with respect to variation of Lead ion concentration, contact time, and pH. To evaluate the effect of varying concentration on the extent of Lead ion uptake by MOF5, 20 mg of MOF5 was mixed with 20 ml of each of 10, 20, 30, 40, and 50 mg/L solutions. In each batch, mixture was stirred for 60 minutes equilibration time. Six contact times, 10, 20, 30, 40, 50 and 60 minutes were studied to evaluate the contact time of maximum uptake. Again, 20 mg of MOF5 and 20 ml of 30 mg/L solution was mixed for each batch. To evaluate the effect of pH, pH of four solutions with concentration 30 mg/L were adjusted using 0.1 M HCl, and 0.1 M NaOH, to pHs of 3, 5, 7, and 8.5 respectively. 20 mg of MOF5 was added to each, and in each batch, continuous stirring was performed for 30 minutes. All solution extracts at the end of each experiment were analyzed with the Flame Atomic Absorption Spectrophotometer (model GBC 908PBMT) to determine the equilibrium concentration of Lead ion.

3. RESULTS

The extent of Lead ions uptake was estimated both in terms of percentage uptake and Lead uptake capacity of MOF5 (Q_e). While percentage uptake was defined as the difference between initial concentrations of Lead solutions (C_0) and concentrations at equilibrium (C_e) according to the relation below:

$$\% \text{ Lead} = \frac{C_0 - C_e}{C_0} \times 100 \%$$

Lead uptake capacity of MOF5 was defined as the weight of Lead ion taken up per gram of MOF5. The weight of Lead ion taken up per gram of MOF5 was estimated by the following relation:

$$Q_e = \frac{(C_0 - C_e) v}{w}$$

where C_0 (mg/L) is the initial concentration, C_e (mg/L) is equilibrium concentration, v is volume of working solution in litre (0.02 ml) and w is weight of MOF5 in gram (0.02 g).

The results are presented in figure one below.

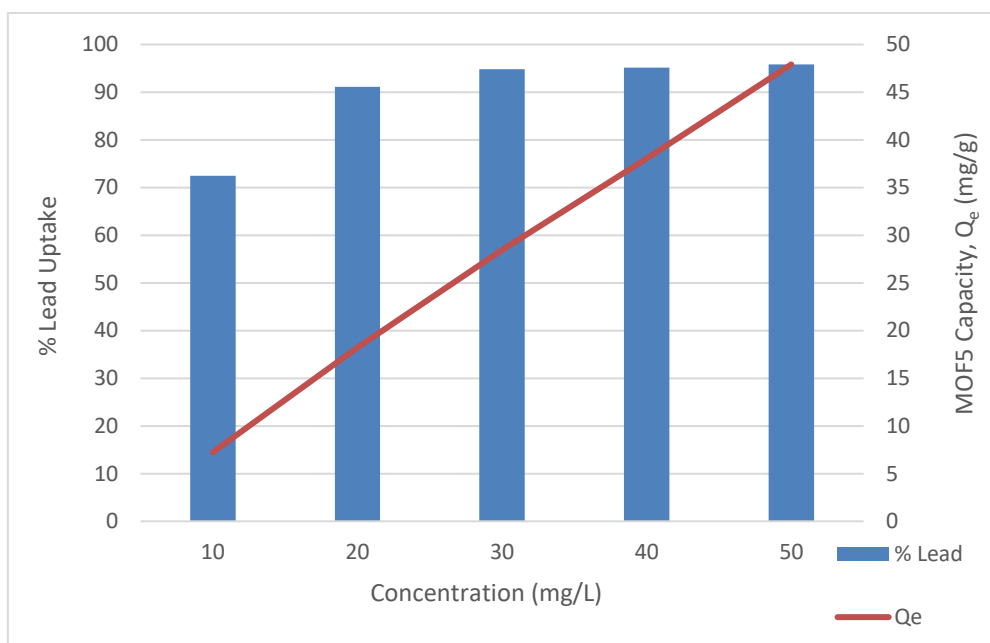


Fig. 1. Charts showing % Lead uptake and capacity of MOF5 to take up Lead ions

Adsorption isotherm models applied to analyse the data obtained from variation of concentration of Lead ion in solution, are shown in Table 1 below. The various isotherm plots are presented in Figures 2 to 6 below.

Table 1. Adsorption Isotherm models

| Isotherm model name | Linear relations | Constants |
|----------------------|--|----------------------------|
| Dubinin-Radushkevich | $\ln Q_e = \ln q_s - K_{ad} \varepsilon^2$ where $\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right]$, $R = 8.314 \text{ J/mol/K}$, $T = 298 \text{ K}$ | $R^2 = 0.2765$ |
| | | $q_s = 6.391 \text{ mg/g}$ |
| | | $K_{ad} = -10^{-6}$ |

| | | |
|------------|---|--|
| | | $E = 1 \div \sqrt{-2K_{ad}} = 0.702$ kJ/mol |
| Langmuir | $\frac{1}{Q_e} = \frac{1}{Q_m K_L C_e} + \frac{1}{Q_m}$ | $R^2 = 0.515$ |
| | | $Q_m = 4.423$ mg/g |
| | | $K_L = -0.677$ |
| Freundlich | $\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e$ | $R^2 = 0.3421$ |
| | | $K_f = 94.29$ |
| | | $\frac{1}{n} = -2.045, n = -0.489$ |
| Jovanovic | $\ln Q_e = \ln Q_m - K_j C_e$ | $R^2 = 0.4229$ |
| | | $Q_m = 200.57$ mg/g |
| | | $K_j = 1.073$ |
| Elovich | $\ln \frac{Q_e}{C_e} = \ln K_e Q_m - \frac{Q_e}{Q_m}$ | $R^2 = 0.8029$ |
| | | $Q_m = -20.080$ mg/g |
| | | $K_e = -0.145$ |

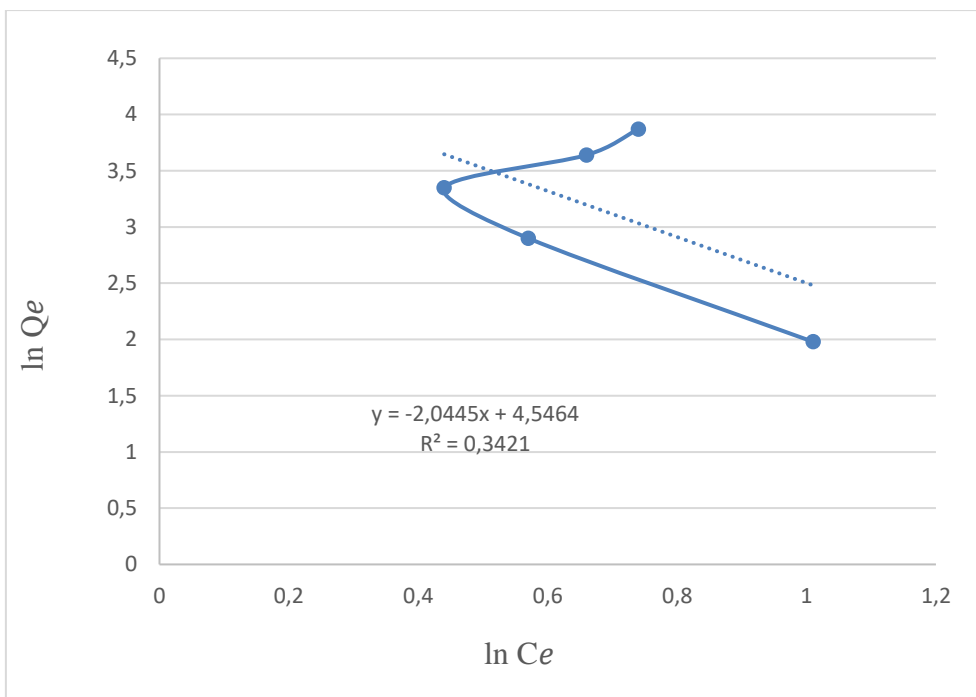


Fig. 2. Freundlich Isotherm Plots

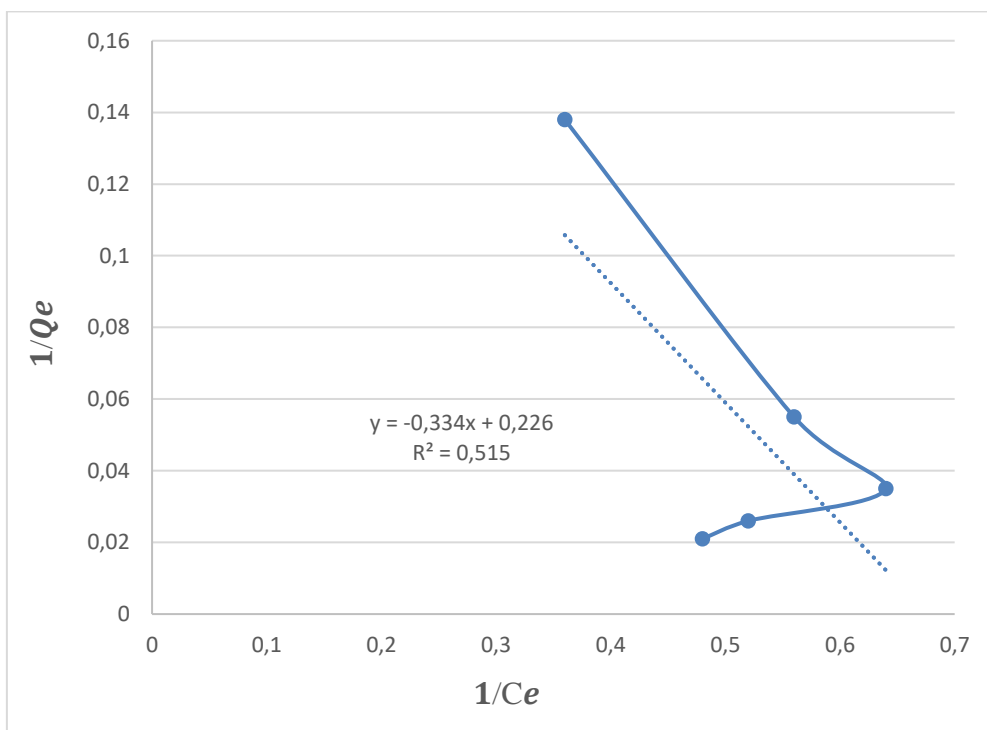


Fig. 3. Langmuir Isotherm Plots

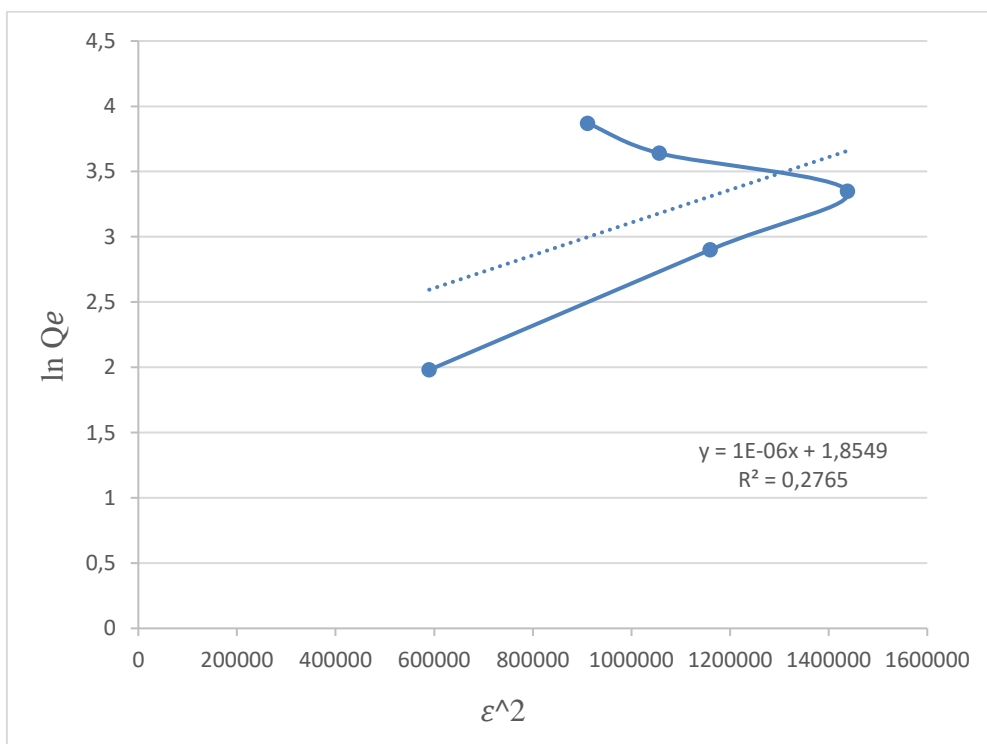


Fig. 4. Dubinin-Radushkevich Isotherm Plots

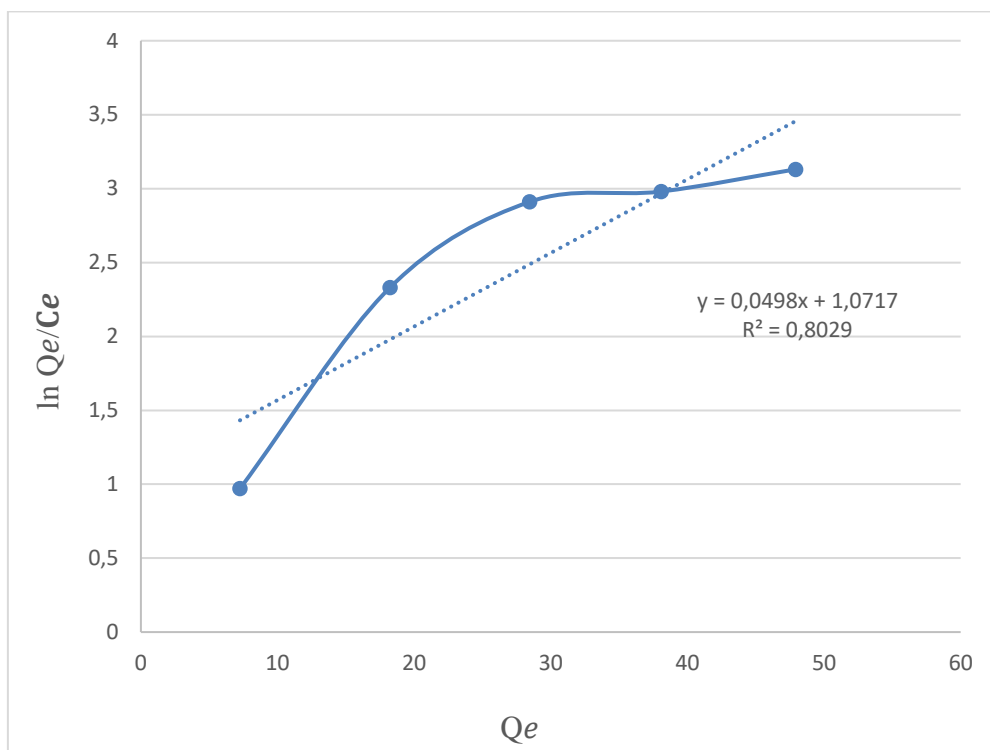


Fig. 5. Elovich Isotherm Plots

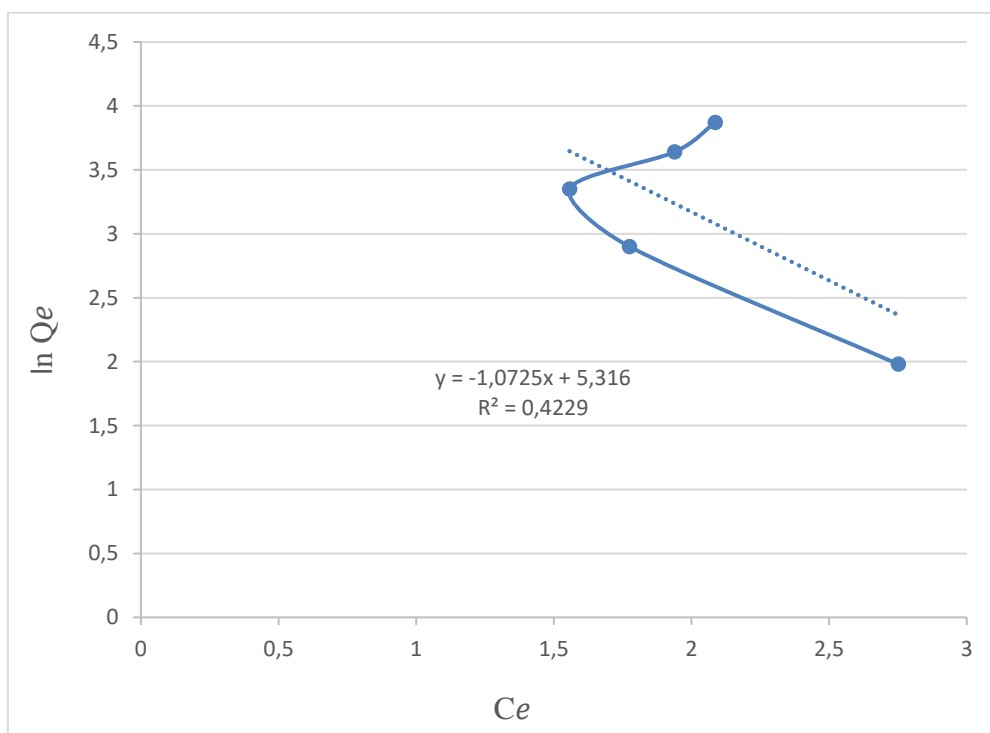


Fig. 6. Jovanovich Isotherm Plots

The results of the study to determine the contact time as well as pH of maximum uptake of Lead ion are presented in Figures 7 and 8 below

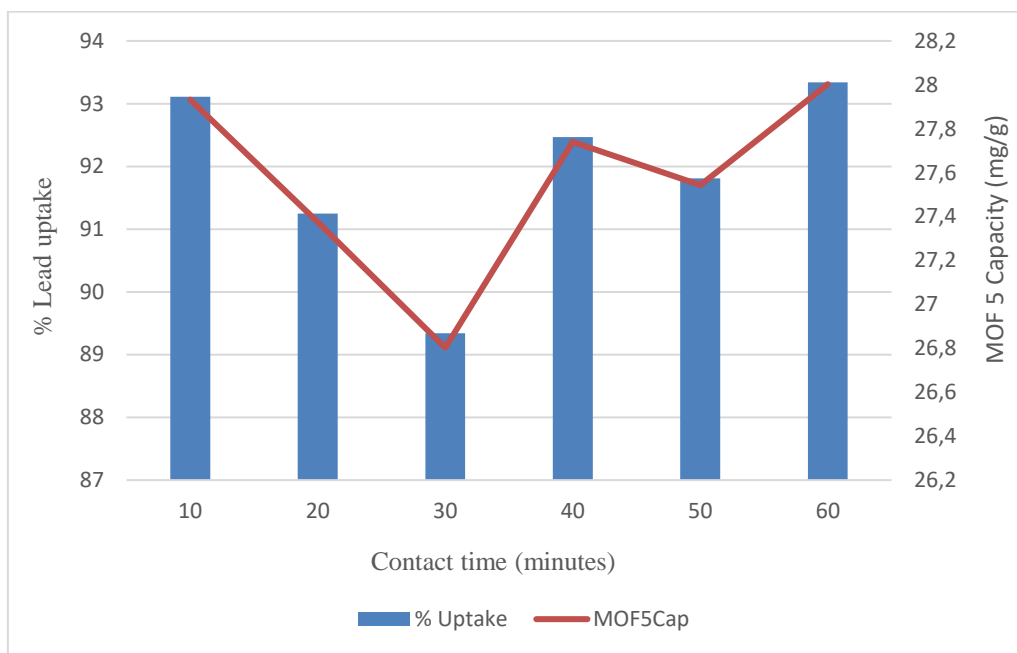


Fig. 7. Effect of contact time on uptake of Lead ion by MOF5

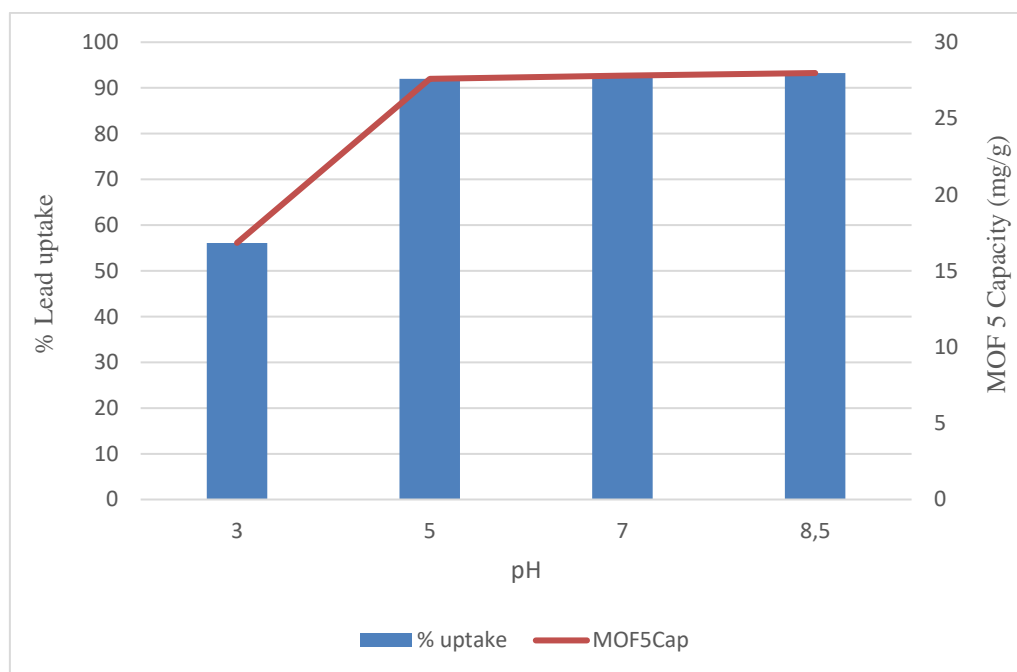


Fig. 8. Effect of pH on uptake of Lead ion by MOF5

The kinetic models applied to analyse the data on contact time and the derived constants are presented in Table 2. The derived plots are presented in Figures 9 and 10.

Table 2. Kinetic model

| Kinetic model | Linear relations | Constants |
|---------------------------------------|---|-------------------|
| Pseudo second-order | $\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e}$ | $R^2 = 0.9992$ |
| | | $K = 0.070$ |
| | | $Q_e = 28.011$ |
| Webber-Morris intraparticle diffusion | $Q_t = K_{i,d} t^{1/2} + X$ | $R^2 = 0.0143$ |
| | | $K_{i,d} = 0.031$ |
| | | $X = 27.389$ |

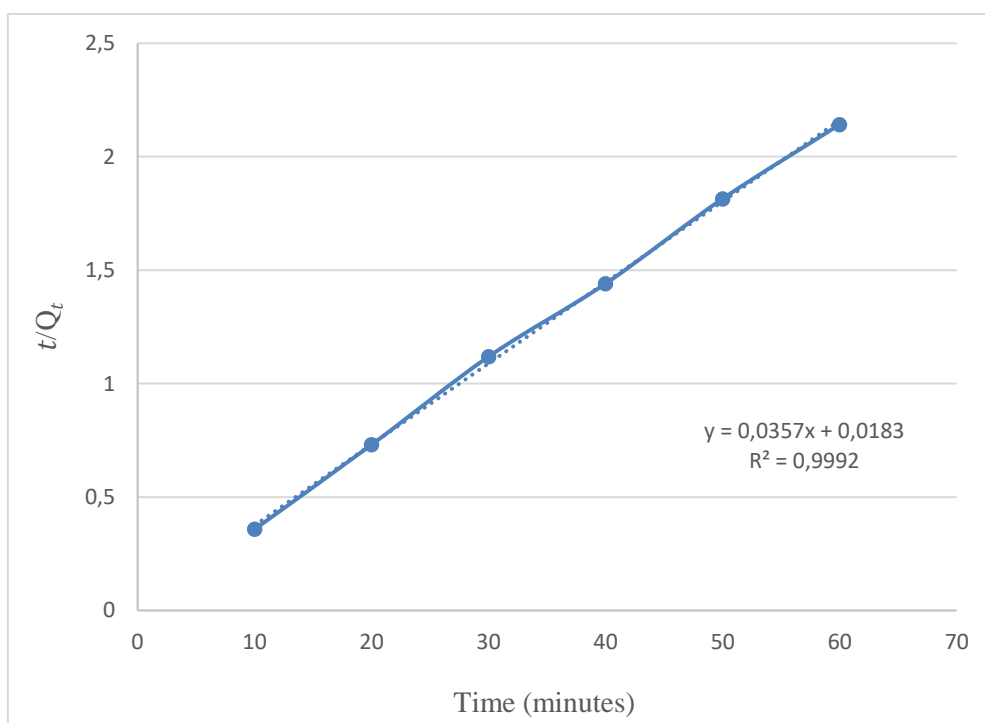


Fig. 9. Pseudo-second order kinetic plots

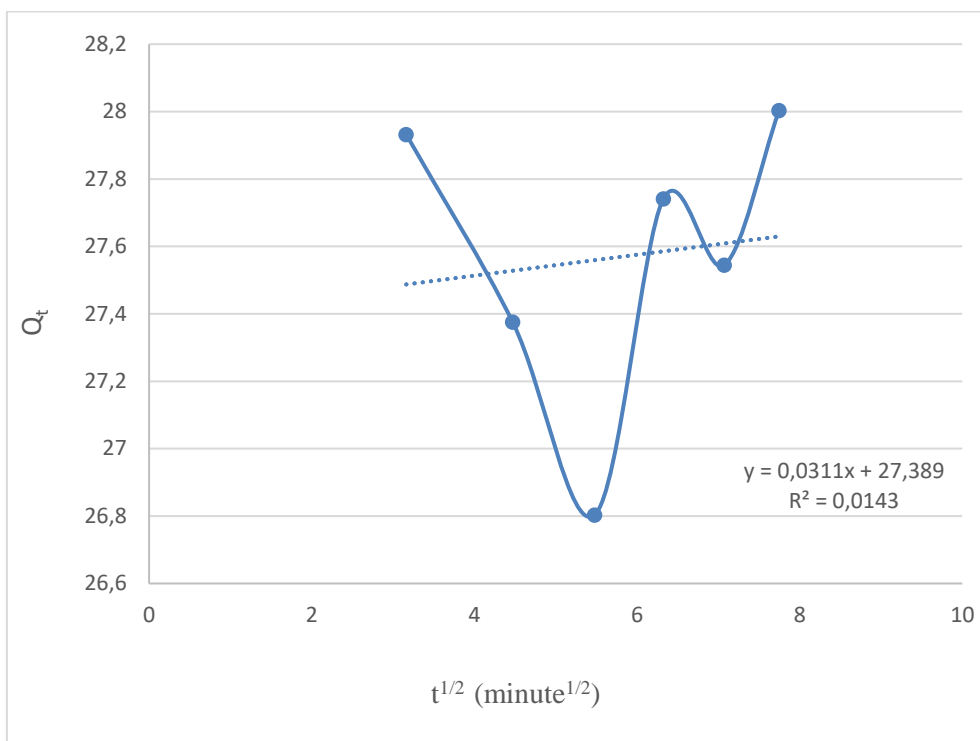


Fig. 10. Webber-Morris Intraparticle diffusion plots

4. DISCUSSION

Effect of concentration: Figure 1 displays the results obtained from the tests to show the effect of concentration on the uptake of Lead ions. It was observed that the percentage of Lead taken up by MOF5 as well as the Lead uptake capacity of MOF5 increased with increase in concentration of Lead ions in solution. However, while the percentage uptake increased steadily and only slightly, the uptake capacity of MOF5 increased steeply, indicating an enhance adsorbate/adsorbent interaction as the solution became more concentrated.

Adsorption isotherm studies: Five adsorption isotherms, Dubinin-Radushkevich, Freundlich, Langmuir, Elovich and Jovanovich models were studied (Table 1). Table 1 reveal the R^2 values from the various isotherm plots as well as the constants derived from the various plots. A comparison of the R^2 values shows that the Elovich isotherm gave R^2 value closest to unity ($R^2 = 0.8029$), hence was the best adsorption model for the uptake of Lead ions by MOF5. The Elovich isotherm is applied to test for the presence of a multilayer adsorption process. The high R^2 value obtained from the Elovich plots reveals that the uptake of Lead ions by MOF5 occurred by a multilayer adsorption process. The average R^2 value obtained from the Langmuir isotherm plots ($R^2 = 0.515$) reveals that a monolayer process had occurred alongside, however, was dominated by multilayer adsorption. One significant function of the Dubinin-Radushkevich isotherm is to determine if an adsorption process occurred by physisorption or chemisorption. The constant E (Table 1) is the adsorption energy derived from the Dubinin-Radushkevich isotherm. If the value of E falls below 8 kJ/mol, the adsorption is physisorption, however, 8 to 16 kJ/mol depicts chemisorption (Mobasherpour et al., 2014). The derived value of 0.702

kJ/mol shows that there was some degree of physiosorptive van der Waals' interactions between Lead ions and MOF5 surfaces.

Effect of contact time: The values obtained from the studies conducted to test the effect of contact time on the performance of MOF5 in the uptake of Lead ions from solutions are presented in the bar charts in figure 7. The values for percentage uptake were 93.11, 91.25, 89.34, 92.47, 91.81 and 93.34 % after 10, 20, 30, 40, 50 and 60 minutes respectively. Those for uptake capacity of MOF5 were 27.932, 27.375, 26.803, 27.741, 27.544 and 28.003 mg/g for 10, 20, 30, 40, 50 and 60 minutes respectively. These values are quite close in magnitude, implying that the effect of contact time was only minimal. The high uptake of Lead ions after just 10 minutes (93.11%) could be explained by the presence of a good number of active sites and pores that could participate in the trapping of the ions as well as the relatively fast kinetics involved in ionic/electrostatic interactions.

Kinetic studies: Two kinetic equations were studied, the pseudo-second order and the Webber-Morris intraparticle diffusion. Based on the R^2 values the pseudo-second order kinetics ($R^2 = 0.9992$) fits the sorption data better than the Webber-Morris model ($R^2 = 0.0143$). Also, the theoretical Q_e value obtained from the pseudo-second-order plots (28.011 mg/g) is almost equal in magnitude to the experimental Q_e value (28.003 mg/g). This shows that the uptake of Lead ion by MOF5 follows the pseudo-second-order kinetics. The pseudo-second-order kinetics is used to explain the presence chemisorptive interactions in an adsorption process. The high R^2 value obtained from the pseudo-second-order plots indicate a chemisorptive interaction involving Lead ions and surface groups on MOF5.

Effect of pH: The percentage uptake of Lead ion and the Lead uptake capacity of MOF5 were observed to increase significantly between pH 3 and pH 5 (Figure 8), however, after pH 5, the increase becomes only slightly with increase in solution's pH. Nevertheless, the results show the significant effect of pH on the uptake of Lead ion. At lower pHs (as seen with pH 3), there are more hydroxonium ions in the solution, and being more reactive than Lead ions, would tend to interact more with the surface groups of the adsorbents. This explains the relatively poorer percentage uptake and Lead ion uptake capacity observed in the solution with pH of 3. The Lead solutions of pH 5 and pH 7 contain fewer hydroxonium ions, however, recorded up to 92 % and 92.71 % uptake respectively. This could be due to the presence of more number of sorption sites on MOF5 that could offset the number of available positive ions in the solution. At pH 8.5, there were more OH⁻ groups in the solution, nevertheless, the higher percentage removal of Lead ions from solution could be a combination of both high pH precipitation of Lead ions, and interactions with MOF5 surface groups.

5. CONCLUSION

The study has demonstrated, through the observed high percentage uptake, that the zinc-based metal-organic framework, MOF5 could represent an efficient adsorbent for consideration, when targeting the sequestration of Lead ions from aqueous media.

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