



Adsorption Study of Lead Ions on Nickel-Metal Organic Framework

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Nickel(II) based metal-organic framework (MOF) was synthesized using terephthalic acid, $C_6H_4(COOH)_2$ as an organic linker. This MOF was characterized and used as an adsorbent for the removal of lead ions in aqueous medium. Characterization was conducted by X-ray diffraction, Fourier transform infrared spectroscopy, thermal gravimetric analysis and scanning electron microscopy techniques. The removal of Pb^{2+} ions from aqueous medium varied with contact time, concentration, pH and temperature.

Keywords: Nickel metal organic framework, Adsorption, Heavy metals, Synthesis, Lead ions.

INTRODUCTION

The pollution of heavy metals in the environment is increasing because of improper disposal of industrial effluents from factories, which manufacture steel, dyes, fertilizers and many others [1]. It is therefore important to remove these pollutants from water. There are various methods used to remove heavy metals from aqueous solutions. Membranes, chemical precipitation and sorbents have been used as remediation methods. However these methods have low efficiency removal of heavy metals, high economic and energy cost, production of large amount of sludge and fouling [2]. These disadvantages have created interest in the use of inexpensive sorbent materials such as metal-organic frameworks. Metal-organic frameworks belong to a class of crystalline compounds containing of metal ions or metal-oxide clusters formed by organic linkers to form three-dimensional structures. These porous materials have been drawing attention due to their internal surface area, large pore sizes, exceptional gas capacity and selective sorption capabilities. Metal-organic frameworks have appeared and these have proved to give multipurpose performances in different research fields, including in adsorptive removal [3] and separation [4]. Thus, the MOFs show great potential as adsorbents for adsorption of heavy metals. Adsorption is one of the efficient and

cost effective methods for removing heavy metals in aqueous solutions [5]. Heavy metals are found in the soil, air, water, in vegetables and flesh of animals. Lead is one of the toxic heavy metals that is used in industries such as metal coating, photographic materials, explosive manufacturing, ceramic and glass manufacturing [6] and it has detrimental effect on metabolic processes of human beings [7] and it has been said that it is carcinogenic agent [8]. It is therefore important to come up with methods to synthesize materials that can be used to remove Pb^{2+} ions. Different adsorbents materials have been synthesized and investigated for their adsorption capabilities [9,10]. Adsorbents such as activated zeolites, clays and carbons they show weak binding affinity towards metal ions [5]. Hence MOFs are used due to their improve sorption capacities [11,12]. In this study Ni-MOF has been chosen as a sorbent material which was prepared using terephthalic acid as an organic linker by conventional heating (reflux) method. The reaction temperature was maintained between 100-104 °C.

EXPERIMENTAL

Methanol (99 %, Promark chemicals), N,N-dimethylformamide (> 99 %, Acros Organics), terephthalic acid (> 99 % Acros Organics), nickel(II) nitrate hexahydrate (99 %, Emsure

ACS), lead nitrate (99 %, Radchem). All chemicals were purchased in Johannesburg South Africa and used without purification.

Synthesis of Ni-MOF: Ni-MOF was synthesized using the method adopted from Shooto *et al.* [13]. A solvent, DMF of 80 mL was transferred into a round bottom flask. A mass of nickel(II) nitrate hexahydrate of 1.04 g with terephthalic acid of 1.03 g were added to the solvent. The flask was connected to the condenser. Heating and stirring of the solution was carried out at 100-104 °C for 24 h. After the reaction had completed, the mixture was centrifuge for 5 min at 5000 rpm. The powder was washed three times with 50 mL of methanol. The powder was dried in the oven at 40 °C for 30 min. The sample was then characterized using different techniques.

Adsorption studies: Lead stock solution (100 ppm) was prepared by dissolving 0.1 g $\text{Pb}(\text{NO}_3)_2$ in 1 L of ultrapure water. Dilution of 60 ppm was made from the stock solution and used as a working solution.

Effect of time: Ni-MOF (0.1 g) weighed in duplicate and transferred into 2 sample vials. Metal ion solution of 10 mL of working solution was added to each weighed sample and equilibrated by agitation for different time intervals of 1, 5, 15, 25, 45, 65 and 85 min. The powered sample suspension was centrifuged for 5 min at 5000 rpm and decanted. The supernatants were stored for Pb^{2+} ions analysis.

Effect of concentration: Ni-MOF (0.1 g) weighed in duplicate and transferred into 2 sample vials. Metal ion solution (10 mL) with standard concentrations of 5, 10, 20, 40, 60 and 80 ppm from stock solution was added to each sample containing the weighed sample and equilibrated by rocking for 45 min and centrifuged at 5000 rpm for 5 min and decanted. The supernatants were stored for Pb^{2+} ions analysis.

Effect of pH: In order to investigate the effect of pH, metal ion solution (100 mL) was added into 5 beakers. The initial pH of each solution was measured and then adjusted to pH of 3, 4, 5, 6 and 7. A solution of 0.1 M of nitric acid and 0.1 M NaOH were used to adjust pH values. A 10 mL of the adjusted pH solutions were added to the 0.1 g sample weighed prior in duplicate. The samples were equilibrated by rocking for 45 min and centrifuged at 5000 rpm for 5 min and decanted. The supernatants were stored for Pb^{2+} ions analysis.

Effect of temperature: Ni-MOF (0.1 g) weighed and placed into 4 sample vials. Metal ion solution of 10 mL of working solution was added to each sample vial containing the weighed sample and equilibrated by rocking for 45 min at temperatures of 30, 40, 50 and 60 °C, respectively, using water bath. The solution was immediately centrifuged at 5000 rpm for 5 min and then decanted. The supernatant was stored for Pb^{2+} ions analysis.

Characterization: The powders were identified using Shimadzu-XRD 700, X-ray diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The scan range was 2θ with continuous scan mode and scan speed of 1 degree per minute using a Cu source at scan range of 15°-80°, current 30 MA and voltage of 40 kV. FTIR spectra were measured using Nicolet iS50 FTIR Spectrometer manufactured by Thermo Fischer Scientific, universal ATR with diamond detector at wavelength from 4000 to 650 cm^{-1} . Thermal studies were determined using Perkin

Elmer, simultaneous thermal analyser STA 6000 with scan temperature from 30 to 900 °C. Temperature ramp rate was 10 °C min^{-1} with nitrogen gas flow of 20 mL min^{-1} . Scanning electron microscopy images were obtained from a Nova Nano SEM 200 from FEI operated at 10.0 kV. Adsorption capacity was conducted using atomic adsorption spectroscopy (AAS) Shimadzu ASC 7000 with auto sampler to determine the remaining Pb^{2+} in the solution.

Data analysis: The adsorption capacity of the studied material in the removal process of Pb^{2+} ions from aqueous medium was calculated by eqn. 1:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where q_e is the amount of Pb^{2+} ions adsorbed on the studied materials (mg/g); C_o and C_e represent the initial and equilibrium concentration of Pb^{2+} ions in the solutions (mg/L), respectively. V is the volume of the solution (L) and m is the mass of the adsorbent (g) used in the experiments.

The removal percent (%) was also calculated using eqn. 2:

$$\text{Removal (\%)} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

The general surface morphology of Ni-MOF composite was confirmed by SEM images shown in Fig. 1(a & b). The images revealed aggregated shaped structures.

X-ray diffraction pattern: Composition and structure of the Ni-MOF were characterized by X-ray diffraction. Fig. 2 shows the XRD pattern of the prepared Ni-MOF sample. The main diffraction peaks are located at 2θ values of 18.2°, 22.1°, 24.6°, 26.8°, 31.2°, 32.2°, 35.2°, 40.6°, 42.8°, 52.8°, 53.3° and 77.6° demonstrating that the Ni-MOF sample is well crystallized.

FT-IR spectroscopy: The FTIR spectrum of Ni-MOF ranging from 4000 and 650 cm^{-1} is shown in Fig. 3. The small peak at 3101 cm^{-1} represent OH absorption. The bands at 1533 and 1384 cm^{-1} are corresponding to the asymmetric and symmetric COO^- stretching vibrations of carboxylates respectively which was also observed in the work of other researchers [14] and the peaks at 824 and 748 cm^{-1} was due to out of plane bending of C-H.

Thermogravimetric analyses: To determine thermal stability of Ni-MOF TGA and DTA plot analyses were carried as shown in Fig. 4. The plots show a two-step weight loss between 72 and 511 °C. The first step between 72 and 183 °C is due to physically adsorbed moisture such as water and methanol that was introduced in the washing step (approximately 20 wt. %) and organic solvent material DMF trapped in the cages of Ni-MOF [6]. The second weight loss of approximately 43 wt. % is observed between 356 and 478 °C. This is due to the collapse of the structures for the sample, indicating that the samples can be stable up to 458 °C which was also observed by Zhao *et al.* [15].

Effect of contact time on the adsorption efficiency: The contact time is important because it influences the adsorption rate of the targeted ions. In order to accomplish the saturation

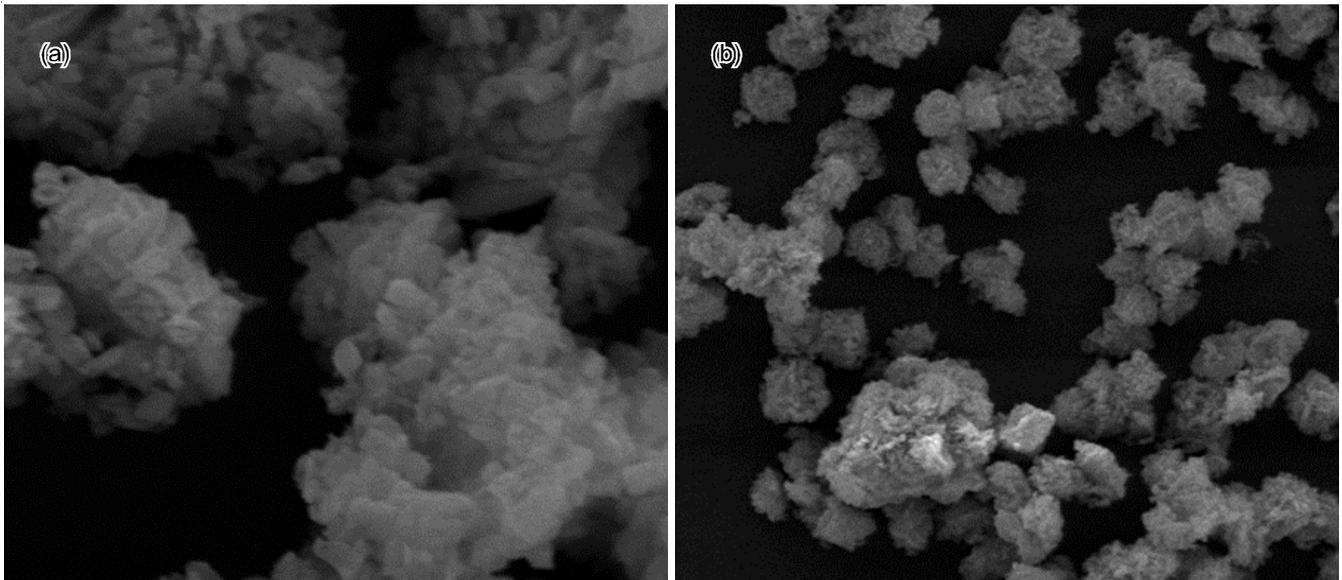


Fig. 1. SEM images Ni-MOF sample

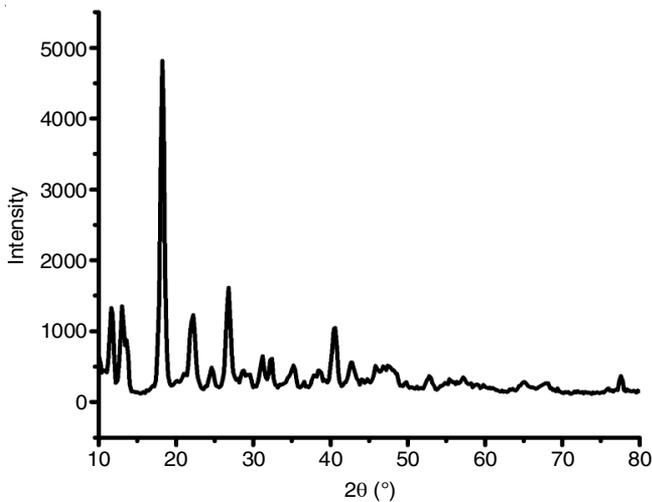


Fig. 2. XRD pattern of Ni-MOF sample

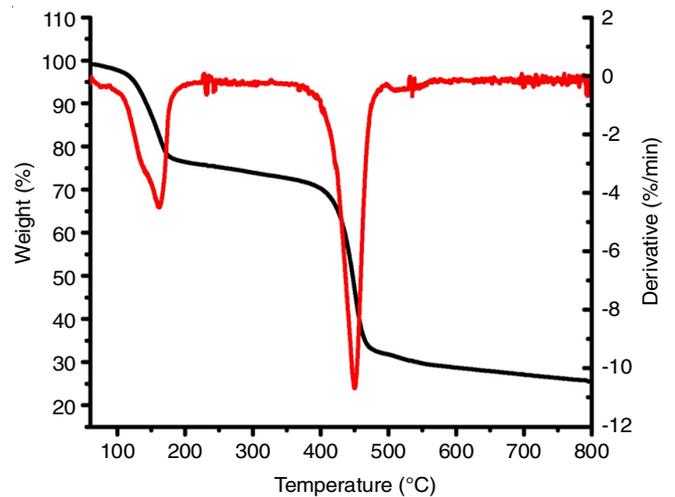


Fig. 4. Thermogravimetric plot of Ni-MOF

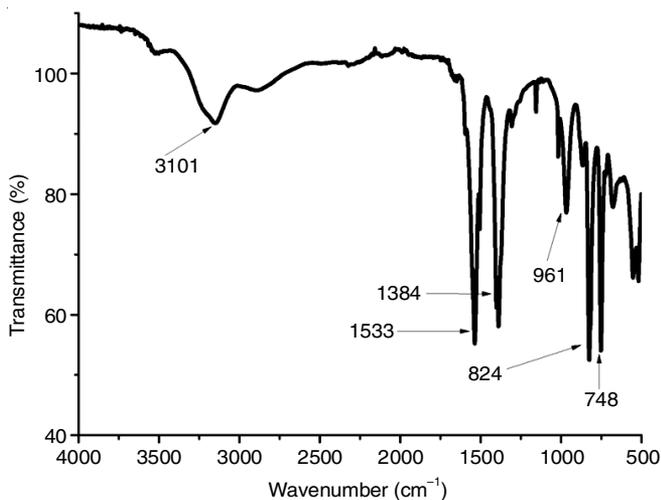


Fig. 3. FTIR spectrum of Ni-MOF

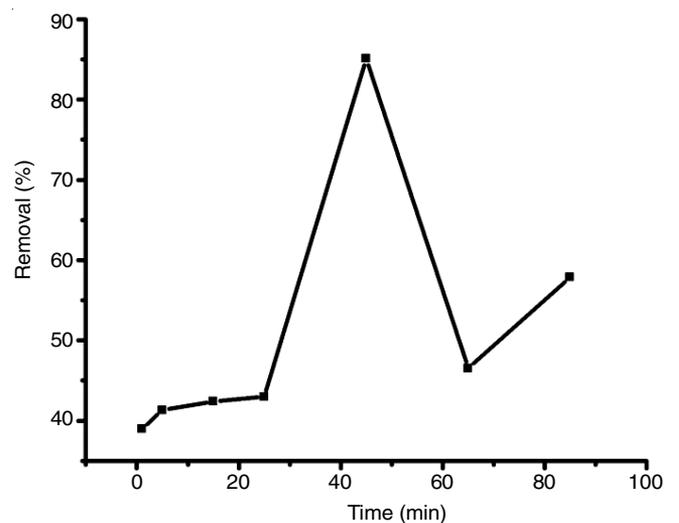


Fig. 5. Effect of time on adsorption of Pb²⁺ ions onto Ni-MOF

uptake removal, the effects of contact time on the adsorption was investigated. Fig. 5 shows the influence of time at 1, 5, 15, 25, 45, 65 and 85 min. The plot shows that the rate of

removal increases steady. The removal of lead ions increases with a maximum removal at 45 min and attain saturation between 45 to 85 min.

Effect of concentration on the adsorption capacity: The percentage sorption of Ni-MOF at different lead ions concentrations of 5, 10, 20, 40, 60 and 80 ppm is shown in Fig. 6. The plot shows that the removal percentages of Pb^{2+} ions increase with the increase of Pb^{2+} concentration, until it reaches equilibrium. This might be due to that the adsorbent had a limited number of active sites, which would have become saturated above certain concentration. This is expected because at lower concentration there is more pore space available for the adsorption to take place, as the concentration of lead ions increases, the adsorption capacity of Ni-MOF decrease due to unavailability of free pores and active sites [6].

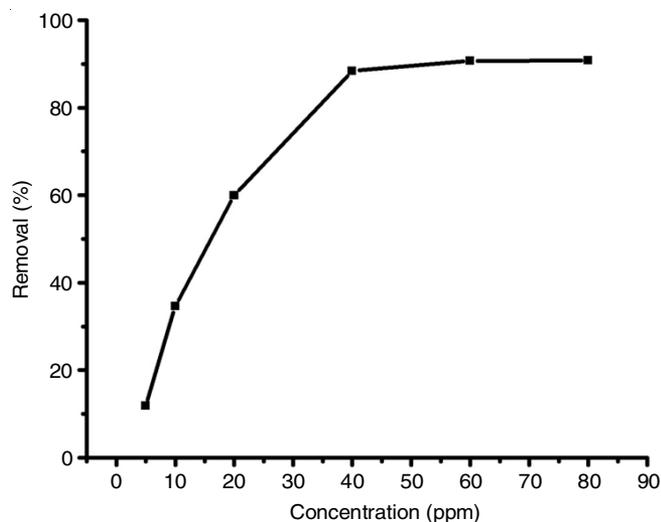


Fig. 6. Effect of concentration on adsorption of Pb^{2+} ions onto Ni-MOF

Effect of pH on the adsorption capacity: The pH of the solution has an influence on the surface properties of the adsorbent and also on the ionic form of the metal solutions [16]. Hence this is the most important parameter for assessing the adsorption capacity of an adsorbent for metal ion removal from aqueous medium. Adsorption experiments were carried out at pH range of 3-7; all other parameters were kept constant. The effect of pH on the adsorption capacity of the material is shown in Fig. 7. The adsorbed amount increases with the increasing in pH from 3.0 to 5.0 with the highest adsorption

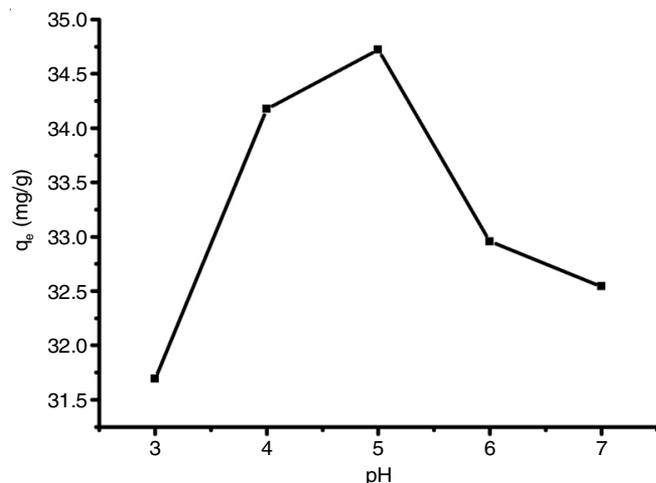


Fig. 7. Effect of pH on adsorption of Pb^{2+} ions onto Ni-MOF

capacity being observed approximately at pH value of 5.3. As the pH increases above pH 5.3 the adsorption capacity decreases. This is due to the surface charge of Ni-MOF at lower pH, which might be positively H^+ charged, thus making ions to compete with metal ions thus causing a decrease in the amount of metal adsorbed [3]. At higher pH, the metal contains lead anion, which was exchanged and had a displacement reaction with NaOH, which might have decreased the adsorption of lead on the Ni-MOF.

Effect of temperature: Fig. 8 illustrates the effect of temperature on Pb^{2+} ions adsorption of Ni-MOF varied at different temperatures of 25, 30, 40, 50 and 60 °C. The figure shows that there is an increase of adsorption from 30 to 60 °C. This steady increase adsorption of lead ions increases with temperature. This could be due to increased kinetic energy of adsorbate and formation of new binding sites on the surface of the material [1].

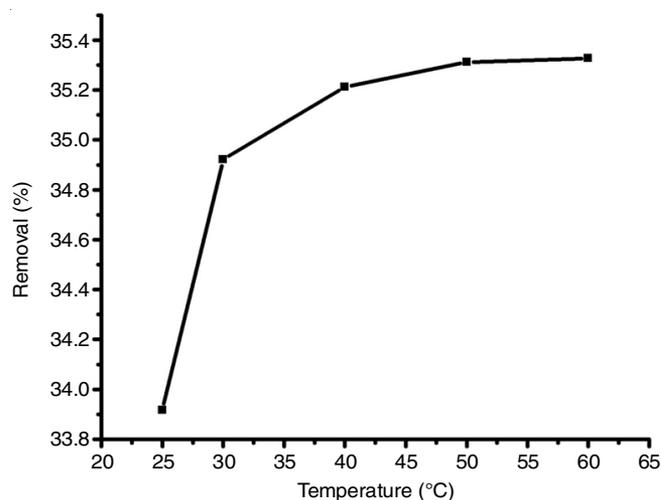


Fig. 8. Effect of temperature on adsorption of Pb^{2+} ions onto Ni-MOF

Conclusion

Ni-metal organic framework was prepared using reflux method and characterized by SEM, XRD, FTIR spectroscopy and TGA. The material showed that it was able to remove lead ions from aqueous solution using experimental conditions. The adsorption results showed that there were depended on time, concentration, pH and temperature. The study showed that the maximum adsorption takes place in an acidic medium. The contact time for the maximum adsorption was observed at 45 min. Ni-MOF has shown to have a potential to be used for the adsorption of lead ions in aqueous solution.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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