In Situ Green Synthesis of Mil-100(Fe) Modified Edta as an Enhanced Candidate Detoxifying Agent of Lead Heavy Metal (Pb) and Its Adsorption Characteristics

Witri Wahyu Lestari (✉ witri@mipa.uns.ac.id)

Universitas Sebelas Maret Fakultas Matematika dan Ilmu Pengetahuan Alam <https://orcid.org/0000-0003-1005-5374>

Rika Meilani

Universitas Sebelas Maret Fakultas Matematika dan Ilmu Pengetahuan Alam

If Nurcahyo

Universitas Sebelas Maret Fakultas Matematika dan Ilmu Pengetahuan Alam

Larasati Larasati

Universitas Sebelas Maret Fakultas Matematika dan Ilmu Pengetahuan Alam

Research Article

Keywords: adsorption, detoxification, EDTA, isotherm, kinetic, MIL-100(Fe), Pb²⁺

Posted Date: September 13th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-810297/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

IN SITU GREEN SYNTHESIS OF MIL-100(Fe) MODIFIED EDTA AS AN ENHANCED CANDIDATE DETOXIFYING AGENT OF LEAD HEAVY METAL (Pb) AND ITS ADSORPTION CHARACTERISTICS

Witri Wahyu Lestari, Rika Meilani, If Nurcahyo, Larasati Larasati

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sebelas Maret, Jl. Ir. Sutami No. 36 A Kentingan, Jebres, Surakarta, 57126, Indonesia

Corresponding author: witri@mipa.uns.ac.id

Abstract:

EDTA-modified MIL-100(Fe) (MIL = Matériaux de l'Institut Lavoisier) was successfully prepared in situ using an electrochemical method. The porous nature of the material and its high stability under intestinal and stomach conditions present it as a great candidate agent for lead detoxification. Kinetic and isotherm investigations revealed that the adsorption of Pb^{2+} ions in MIL-100(Fe)-EDTA followed a pseudo-second order kinetic model with a rate constant of 0.0109 g/mg.min and a Langmuir isotherm model with an adsorption energy of 31.29 kJ/mol. The synthesized MIL-100-EDTA showed three times enhanced performance than MIL-100(Fe) in Pb^{2+} adsorption study. Optimum adsorption was achieved at pH 3 at an initial concentration of 5 ppm and a contact time of 12 h, yielding adsorption efficiency and capacity of up to 86.65% and 3.68 mg/g, respectively.

Keywords: adsorption, detoxification, EDTA, isotherm, kinetic, MIL-100(Fe), Pb^{2+}

Introduction

The increasing use of lead in various products, including dye, paint, ceramics, glasses, jewelries, and toy industries, gives rise to the high exposure of the environment and humans to heavy metals. The World Health Organization categorized lead as one of the main chemical causes of health problems (Sun 2018). It can easily enter the human body via ingestion, inhalation, or skin contact (Zhou 2018, Forghani 2020). The maximum permissible level of Pb^{2+} in water is 0.01 mg/L. Lead intoxication commonly occurs because of accumulation in the human body due to its long half-life and non-biodegradable nature. Lead poisoning causes severe damage, such as heart disease, cancer, anemia, and liver failure, as well as gastrointestinal, kidney, and brain damage, even at very low concentrations (Wang 2016, Zhu 2019). Lead detoxification to remove hazardous metals from the human body can be carried out by several techniques, including chemical precipitation, electrochemistry, flocculation, adsorption, and membrane separation, but one of the most effective is adsorption using adsorbent materials (Zhu 2019).

Metal-organic frameworks (MOFs) are three-dimensional porous hybrid materials constructed by inorganic cluster nodes and organic ligands as the linkers. The ultrahigh porosity of MOFs makes them a great candidate as adsorbents in lead detoxification. One of the most widely-used MOFs, due to their non-toxicity and biocompatibility in biomedical applications, including drug delivery and detoxification, is MIL-100(Fe) ($\text{Fe}_3\text{F}(\text{H}_2\text{O})\text{O} [\text{C}_6\text{H}_3(\text{CO}_2)_3]_2.n\text{H}_2\text{O}$) (MIL = Matériaux de l'Institut Lavoisier) (Horcajada *et al.*, 2007; Nguyen *et al.*, 2019). It contains $[\text{Fe}_3\text{O}(\text{X})(\text{H}_2\text{O})_2]^{6+}$ clusters interconnected by 1,3,5-benzenetricarboxylate ligands that generate permanent pentagonal and hexagonal cavities (25 Å and 29 Å) with microporous windows of 5.5 Å and 8.6 Å (Bezverkhyy *et al.*, 2016; Huo *et al.*, 2012). In addition to the porosity, MIL-100(Fe) possesses a large surface area and high thermal and chemical stability (Shi *et al.*, 2013; Han *et al.*, 2017; Yuan *et al.*, 2019). The presence of unsaturated open metal sites in the framework allows coordination with various compounds, such as EDTA.

Ethylenediaminetetraacetic acid (EDTA) is an effective chelating agent with four carboxyl and two tertiary amine sites, and it can effectively extract Pb^{2+} ions from contaminated soil (Lim 2005). A previous report showed that the coordination of EDTA into support materials could maintain active functional sites (Wu *et al.*, 2019). Several studies have been conducted to immobilize EDTA to support materials for Pb^{2+} adsorption, such as EDTA-GO (Madadrang *et al.*, 2012), MOF-808-EDTA (Peng *et al.*, 2018), and UiO-66-EDTA (Wu *et al.*, 2019), and have shown

enhanced adsorption capacity. Mostly, MIL-100(Fe) is synthesized under hydrothermal or solvothermal reactions in the presence of HF as a modulator that is not environmentally friendly (Horcajada *et al.*, 2007; Nguyen *et al.*, 2019) and has not yet been modified with EDTA or investigated for lead detoxification. Moreover, the integration of EDTA into previously mentioned MOFs was achieved through the long post-synthesis method, which required high energy, longer reaction time, and poor chemical stability (Wu *et al.*, 2019; Zhang *et al.*, 2021). In this study, we successfully modified MIL-100(Fe) with EDTA in situ to open metal sites via the green electrochemical method with a shorter reaction time at ambient temperature, and evaluated the performance of the material in the Pb²⁺ detoxification.

Experimental

Materials

The materials used in this study were Fe electrodes (dimension 10 × 0.1 × 0.5 cm; Pudak Scientific, 99.9%), H₃BTC (Sigma Aldrich, 95%), EDTA-2Na (Merck, 99%), ethanol (Sigma Aldrich, 96%), tetra-butyl ammonium tetra-fluoroborate (TBATFB) (Sigma Aldrich, 98%), Pb²⁺ solution 1000 ppm (Merck), phosphate buffer saline (PBS) solution (pH 7.2), acetone (Merck, 99%), HNO₃ (Merck, 65%), NaOH (Merck, 97%), concentrated HCl (Mallinckrodt, 37%), NaCl (Merck, 99%), NaHCO₃ (Riedel-deHaen, 99%), MgCl₂·6H₂O (Merck, 99%), CaCl₂ (Merck, 99%), K₂HPO₄·3H₂O (Merck, 98%) and KH₂PO₄ (Merck, 99%). All materials were used as purchased without further purification.

Synthesis of MIL-100(Fe) and MIL-100(Fe)-modified EDTA

MIL-100(Fe) was synthesized via an electrochemical method. Fe electrodes were cleaned using sandpaper, washed with HNO₃ (1 M), and rinsed with water. The H₃BTC ligand (0.1 M) and TBATFB electrolyte were dissolved in 50 mL of water: ethanol (1:1) and stirred. The Fe electrodes were then placed in a beaker containing the solvent and electrolyte mixture. Electrolysis was conducted at room temperature for 2 h at a voltage of 15 V. The obtained brown solid was filtered, washed twice with ethanol to remove the residual ligand, and dried at room temperature, followed by activation at 200°C for 2 h.

MIL-100 (Fe)-EDTA was prepared in situ using the same method as MIL-100 (Fe) but with the addition of EDTA (H₃BTC: TBATFB: EDTA-2Na = 1:1:1). The obtained solid was

washed with water (2 × 25 mL) and ethanol (2 × 25 mL), dried at room temperature, and activated at 60°C for 12 h.

Characterization

X-ray diffractograms were recorded using X'Pert Pro MPD with Cu K- α ($\lambda = 1.5418 \text{ \AA}$) radiation to observe the crystallinity and phase purity synthesized materials. FTIR spectra were measured using Shimadzu-type IR Prestige-21 to analyze the shift in functional groups of the materials. Thermogravimetry analysis was performed using Hitachi STA-7000 with a heating rate 10°C/min under nitrogen flow. The surface area, pore volume, and pore size distribution were measured using Quantachrome QuadraSorb Station 3 Version 5.04. The SEM and TEM analyses were performed on Hitachi SU-3500 and Jeol Jem-1400, respectively, to observe the morphology of the synthesized materials.

Adsorption Studies

Effectivity Test of the Adsorbent Materials

The effectivity of the material in adsorbing Pb was measured by immersing 10 mg of the adsorbent (MIL-100(Fe) or MIL-100(Fe)-EDTA) into 10 mL of Pb(NO₃)₂ (5 ppm) at a pH of 1.2. The mixture was shaken at 240 rpm for 24 h to achieve adsorption equilibrium, and then filtered. The concentration of Pb(NO₃)₂ in the filtrate was analyzed by atomic adsorption spectrometry (AAS) to identify the equilibrium concentration of Pb²⁺ ions (C_e). The number of the adsorbed Pb²⁺ ions was determined from the difference between the initial concentration and equilibrium concentration of Pb²⁺ ions in the solution. The efficiency and adsorption capacity were then calculated using Equations 1 and 2 (Jin *et al.*, 2019).

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

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

where q_e is the adsorption capacities of the ions in the adsorbent (mg/g), V is the volume of the Pb(NO₃)₂ solution (L), C_o is the initial concentration of Pb(NO₃)₂ solution (mg/L) and C_e is the equilibrium concentration of Pb(NO₃)₂ solution (mg/L).

Effect of pH, Contact Time, and Initial Concentration on Pb²⁺ Adsorption

Optimization to determine the optimum condition for Pb^{2+} adsorption was conducted by mixing 10 mg of MIL-100(Fe)-EDTA as the adsorbent and 10 mL of $\text{Pb}(\text{NO}_3)_2$. To evaluate the effect of pH, PBS solution was added, and the pH was tuned to 1.2, 2, 3, 4, 5, 6, 6.8, and 8.2. Using the obtained optimum pH, the optimum contact time was determined by varying the contact time at 15, 30, 60 min and 3, 6, 9, 12, 15, 24 h. The optimum initial concentration was evaluated with a range of 2, 5, 10, 20, and 30 ppm. The mixture of adsorbent and $\text{Pb}(\text{NO}_3)_2$ solution was shaken at 140 rpm for 24 h and then filtered, and the Pb^{2+} content was analyzed using AAS.

Results and Discussion

Materials Characterization

X-Ray Diffraction (XRD)

MIL-100(Fe) and MIL-100(Fe)-EDTA were successfully synthesized via the electrochemical method, as confirmed by XRD analysis. The diffractogram (Figure 1 and ESI Figure S1) showed similar characteristic peaks between the as-synthesized materials and the standard pattern of MIL-100(Fe) (CCDC No.640536) at $2\theta = 6.29^\circ$ (511); 7.08° (440); 10.22° (660); 11.0° (428); 12.74° (1022); 14.83° (088); 20.09° (4814); 24° (6618); and 27.5° (9312). The diffractogram of EDTA-modified MIL-100(Fe) (Figure 1) also displayed high similarity compared to both MIL-100(Fe) ($2\theta = 6.22^\circ$ (511); 6.72° (404); 10.22° (660); 10.95° (428); 12.47° (1022); 14.63° (088); 20.06° (4814); 24.0° (6618); and 27.90° (9321)) and EDTA-2Na (JCPDS File No. 29-1917) ($2\theta = 11.03^\circ$ (020); 17.39° (002); 26.28° (430); and 29.25° (422)).

Figure 1. Diffractogram of the as-synthesized MIL-100(Fe)-EDTA compared to the as-synthesized and standard pattern (CCDC No. 64053) of MIL-100(Fe) and EDTA-2Na (JCPDS No. 29-1917)

Fourier Transform Infrared Spectroscopy (FTIR)

The successful synthesis of MIL-100(Fe)-EDTA was also confirmed by FTIR analysis. The characteristic bands from the COOH groups in H₃BTC spectra (ν_{OH} , 3087 cm^{-1} ; $\nu_{\text{C=O}}$, 1719 cm^{-1} ; $\delta_{\text{C=O}}$, 1275-1109 cm^{-1}) disappeared and shifted in the MIL-100(Fe) spectra (Maiti *et al.*, 2015). As depicted in Figure 2, the absorption band of carboxyl groups (C=O) shifted from 1719 cm^{-1} to 1623 cm^{-1} , indicating the deprotonation of the ligand and coordination with Fe^{3+} ions, which was also supported by the presence of the absorption band of Fe-O bonds at 473 cm^{-1} . The change in the absorption of O-H carboxyl from 3087 cm^{-1} - 2553 cm^{-1} in H₃BTC to 3403-3084 cm^{-1} in the as-prepared MIL-100(Fe) indicated the formation of molecular bonds between H₂O and Fe^{3+} ions. Vibration bands of the O-C-O groups were observed at 1445–1377 cm^{-1} , and the absence of C=O stretching vibration in the MIL-100(Fe) spectra showed that the residual ligand was completely removed by the ethanol washing procedure (Huang *et al.*, 2017).

The FTIR spectra of MIL-100(Fe)-EDTA (Figure 2) was similar to the spectra of the unmodified MOFs. New peaks were observed at 1005 cm^{-1} , 2876 cm^{-1} and 2964 cm^{-1} that represented C-N, C-H, and N-H bonds, confirming the coordination of EDTA in MIL-100(Fe) (Zhang *et al.*, 2019). The relatively low peaks of C-N bonds at $1042\text{--}1000\text{ cm}^{-1}$, C-H bonds at $2890\text{--}2850\text{ cm}^{-1}$ and N-H bonds at $2990\text{--}2940\text{ cm}^{-1}$ in the MIL-100(Fe)-EDTA spectra resembled the small amount of EDTA added to the MOFs.

Figure 2. FTIR Spectra of MIL-100(Fe) and MIL-100(Fe)-EDTA compared to H₃BTC ligand

Thermo Gravimetric Analysis (TGA)

Thermal stability of the materials was measured using thermogravimetry analysis (TGA), revealing three mass losses in the temperature range of 25–500°C (see ESI Figure S2). The first mass loss of 24.9% and 23.3% for MIL-100(Fe) and MIL-100(Fe)-EDTA, respectively, occurred at 25–150°C and was related to the evaporation of water and ethanol solvents both on the surface and within the porosity of the materials. Further calculations showed that 12 and 15 molecules of water were removed from MIL-100(Fe) and MIL-100(Fe)-EDTA, respectively.

A second mass loss was observed at 100–348°C, with a loss of 4.5% and 5.3% for MIL-100(Fe) and MIL-100(Fe)-EDTA, respectively, indicating the removal of the two and three water molecules coordinated to the Fe trimmers. This is in agreement with the structure of MIL-100(Fe), which binds two water molecules (Abednatanzi *et al.*, 2017). In the MIL-100(Fe)-EDTA, the second mass loss also corresponded to the removal of EDTA. According to Narayanan *et al.* (2015), EDTA began to decompose at 230–320°C, resulting in a mass loss of up to 70%. The third mass loss at 300–500°C was 28.4% for MIL-100(Fe) and 25.1% for MIL-100(Fe)-EDTA, which was associated with the degradation of the frameworks. The total mass loss of MIL-100(Fe)-EDTA was slightly lower than that of MIL-100(Fe) due to the attachment of EDTA. Overall, the TG curve showed that the thermal stability of the materials was up to 308°C for MIL-100(Fe) and 348°C for MIL-100(Fe)-EDTA. The higher stability of MIL-100(Fe)-EDTA is related to the strong coordination between the metal nodes and carboxyl groups in EDTA (Abednatanzi *et al.*, 2017).

Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX) and Transmission Electron Microscopy (TEM)

The morphology of the synthesized materials was analyzed using SEM-EDX and TEM. A study by Forghani *et al.* (2020) demonstrated that MIL-100(Fe) occupies octahedral geometry, whereas in this study, it showed an irregular shape, as seen from the results of SEM imaging (Figure 3a). Seo *et al.* (2012) reported that the use of HF in the synthesis of MIL-100(Fe) could improve the crystallinity since the F⁻ anions have the capability to stabilize the Fe³⁺. However, the electrochemical method we used in this study did not include HF as a modulator, which is the reason for the irregular morphology of the products. In this case, F⁻ anions were replaced by hydroxyl anions (from water) to balance the charge of Fe³⁺.

Figure 3. SEM imaging of MIL-100(Fe) (a) and MIL-100(Fe)-EDTA (b) TEM imaging of MIL-100(Fe) (c) and MIL-100(Fe)-EDTA (d) TEM imaging of MIL-100(Fe) (e) and MIL-100(Fe)-EDTA (f) after Pb^{2+} ions adsorption (red circle shows the presence of Pb^{2+})

As shown in Figure 3b, the EDTA modification yielded no significant difference in the morphology but slightly increased the particle size. The average particle sizes of MIL-100(Fe) and MIL-100(Fe)-EDTA were $0.90 \pm 0.30 \mu\text{m}$ and $0.94 \pm 0.32 \mu\text{m}$, respectively. The histogram of particle size distribution showed that the particle size ranged from 0.29 to 1.68 μm for MIL-100(Fe) and from 0.31 to 1.72 μm for MIL-100(Fe)-EDTA (see ESI Figure S3). The particle size of the materials in this study was smaller than those reported in the literature, which ranged from 0.4 to 8.6 μm (Lestari *et al.*, 2016).

The TEM images, however, showed that the geometry of both MIL-100(Fe) and MIL-100(Fe)-EDTA was nearly octahedral (Figure 3c). Micrograph of TEM MIL-100(Fe)-EDTA (Figure 3d) revealed that some of the MIL-100(Fe) were planted around the EDTA according to the number of EDTA added in the reaction. This indicates that EDTA was coordinated into the surface of MIL-100(Fe). The histogram in ESI Figure S4 demonstrates that the particle size of MIL-100(Fe) ranged from 137 to 227 nm, whereas for MIL-100(Fe)-EDTA, it was 127–203 nm. The morphology of both materials showed no significant change after exposure to the $\text{Pb}(\text{II})$ solution

during the adsorption process (Figure 3e). The successful adsorption of Pb was proven by the entrapped Pb(II) molecules within the MOFs, shown in the red circles in Figure 3f, with no change in the morphology of the host material. This phenomenon shows that MIL-100(Fe) and MIL-100(Fe)-EDTA can be used as adsorbents (detoxification agent) for Pb²⁺ metal ions.

Surface Area Analyzer (SAA)

Figure 4. Nitrogen sorption isotherm (a) and pore size distribution (b) of MIL-100(Fe) and MIL-100(Fe)-EDTA

Nitrogen adsorption-desorption isotherm curves showed that both MIL-100(Fe) and MIL-100(Fe)-EDTA, according to the IUPAC classification, followed a type I isotherm that indicated microporosity (Figure 4a). MIL-100(Fe) had the BET surface area of 722.433 m²/g and pore volume of 0.025 cc/g. Its surface area is higher than that of MIL-100(Fe) synthesized by Lestari *et al.* (2016), but the pore volume is lower (surface area of 569.191 m²/g with pore volume of 0.4540 cc/g). The addition of EDTA to MIL-100(Fe) decreased its BET surface area to 587.253 m²/g. Thus is in accordance with the report by Wu *et al.* (2019) that demonstrated the same phenomenon, since the EDTA molecules block the porosity of MOFs. However, the surface area is still larger than other adsorbent materials, such as polyethylenimine-modified activated carbon (363 m²/g) (Saleh *et al.*, 2017), silica/lignin (223 m²/g) (Klapiszewsk *et al.*, 2015), Al₂O₃ (346 m²/g)

(Akarmazyan *et al.*, 2014), and ascorbic acid-Fe₃O₄ (178 m²/g) (Feng *et al.*, 2012). However, its porosity slightly increased to 0.128 cc/g. The micropore size in the materials was also measured using the Barrett, Joyner and Halenda (BJH) method. Figure 4b illustrates the pore size distribution of MIL-100(Fe) and MIL-100(Fe)-EDTA, revealing a pore radius of 1.7 nm and 1.9 nm for both materials, respectively.

Stability Test of Materials in the Intestinal and Stomach Simulation Medium and Water

The stability of MIL-100(Fe) and MIL-100(Fe)-EDTA was tested in a water medium at pH 7, Ringer's solution at pH 6 to simulate the intestinal medium, and a hydrochloride acid solution (HCl) at pH 1.2 to simulate the stomach medium, according to the procedure described by Rojas *et al.*, (2018). The FTIR spectra for the materials in the corresponding mediums after a period (24 h for intestinal simulation and 2 h for stomach simulation at room temperature) demonstrated no significant change (see ESI Figure S5). The new absorption band appearing in the intestinal simulation spectra is a result of the presence of PO₄³⁻ ions in the intestine (Mobasherpour *et al.*, 2007; Rojas *et al.*, 2018).

The XRD of the materials after the stability test also validated the results. As shown in Figure 5, the characteristic peak at $2\theta = 11^\circ$ for each material was maintained after contact with the mediums (Forghani *et al.*, 2020), proving that the materials have high stability. However, in the intestinal simulation medium, the peaks of both MIL-100(Fe) and MIL-100(Fe)-EDTA displayed different intensities when compared to the other medium. This is because in the digestion system, various ions (such as phosphate in the intestine), enzymes, and entities compete with the building blocks of the frameworks, thus decreasing their crystallinity (Rojas *et al.*, 2018).

Figure 5. X-Ray diffractograms of MIL-100(Fe) (A) and MIL-100(Fe)-EDTA (B): initial materials (a) and after the stability test in water medium (b), stomach simulation medium (c), and intestinal simulation medium (d)

Lead Removal Study

Preliminary test of Pb²⁺ Adsorption Effectivity of MIL-100(Fe) and MIL-100(Fe)-EDTA

A preliminary effectivity test was conducted to evaluate the adsorption efficiency and capacity of MIL-100(Fe) and MIL-100(Fe)-EDTA to detoxify Pb²⁺ by immersing the materials in Pb(NO₃)₂ solution (5 ppm) at pH 1.2 for 24 h after adsorption equilibrium was achieved. The results are depicted in Figure 5.

Figure 6. Adsorption efficiency of MIL-100(Fe) and MIL-100(Fe)-EDTA against Pb²⁺ in Pb(NO₃) 5 ppm solution for 24 h

MIL-100(Fe)-EDTA showed higher adsorption efficiency and capacity than MIL-100(Fe). The efficiency of MIL-100(Fe)-EDTA was almost three times higher than that of MIL-100(Fe), with adsorption capacities of 0.87 mg/g and 0.32 mg/g for both materials, respectively. The higher adsorption capacity found in MIL-100(Fe)-EDTA may be related to the presence of the chelating agent EDTA, which forms a strong chelation with Pb²⁺ ions (Peng *et al.*, 2018). In addition, the carboxyl groups from EDTA increase the number of active sites in the MOFs, hence improving the adsorption capacity (Luo *et al.*, 2015). The interaction between MIL-100(Fe)-

EDTA with Pb^{2+} ions is illustrated in Figure 7, in which every EDTA molecule acts as a Lewis base and binds to one Pb^{2+} ion (Peng *et al.*, 2018).

Figure 7. Predicted interaction between MIL-100(Fe)-EDTA and Pb^{2+} ions

Figure 8. Effect of pH on the Pb^{2+} ions adsorption efficiency

One of the critical parameters in the adsorption process is the pH of the solution. Initial pH determination is mandatory since it could affect the chemical properties of the adsorbent and the ion species existing in the solution (Zhou *et al.*, 2018). The effect of pH is also correlated with the ionization state of the functional groups in the adsorbent, which further affects the number of

active binding sites (Elsayed *et al.*, 2016). The results of the Pb adsorption efficiency of MIL-100(Fe)-EDTA with varied pH levels of 1.2, 2, 2.3, 4, 5, 6, 6.8, and 8.2 for 24 h are shown in Figure 8.

The optimum condition was achieved at a pH of 3, with adsorption efficiency and capacity of 94.24% and 1.63 mg/g, respectively, while the lowest efficiency was found at a pH of 1.2. This is because at a lower pH, the H^+ ions compete with the Pb^{2+} ions to interact with the adsorbent, leading to lower adsorption. Beyond pH 1.2, however, the trend followed that of a previous study in which the maximum adsorption efficiency of Pb^{2+} ions was found at low pH, and the value decreased as the pH increased. The decreasing adsorption efficiency at increasing pH showed that the adsorption mechanism most likely occurred via chemical interaction or substitution process instead of electrostatic forces (Goyal *et al.*, 2021). The optimum adsorption of Pb^{2+} in MIL-100(Fe), as reported previously by Forghani *et al.* (2020), was ~65% at a pH 5.5. Greater Pb^{2+} adsorption efficiency of MIL-100(Fe)-EDTA supports the previous result that EDTA increases the number of active sites of the adsorbent and consequently improves the adsorption capacity. Fluctuated curve at a pH range of 4–8.2 is related to the structure of the MOFs that have characteristic acid and base sites that could be activated by tuning the pH (Rivera *et al.*, 2016).

Effect of Contact Time

The adsorption performance of MIL-100(Fe)-EDTA was evaluated as a function of time. Measurement was conducted in 10 mL of $Pb(NO_3)_2$ solution (5 ppm) at an optimum pH of 3, with a treatment period that ranged from 15 min to 24 h. Adsorption efficiency tended to rise as the contact time increased, dropping at 6 h and remaining constant after 24 h (**Figure 9**). Equilibrium was achieved at 12 h with efficiency and capacity of 82.79% and 3.23 mg/g. After 12 h, no significant change was observed, indicating that Pb^{2+} ions fully occupied the active sites of the adsorbent material.

Figure 9. Effect of contact time on the Pb^{2+} ions adsorption efficiency

Effect of Lead Concentration

Different concentrations of $Pb(NO_3)_2$ solutions, 2, 5, 10, 20, and 30 ppm, were prepared to compare the effect of the initial concentration on adsorption efficiency and capacity of the MOFs, as profiled in Figure 10. High adsorption of up to 86.65% was observed in the solution with an initial concentration of 5 ppm.

The adsorption capacity increased significantly with increasing concentrations of Pb^{2+} , as indicated by the large number of ions adsorbed per area of adsorbent. Furthermore, the large number of ions is also the driving force for the transfer of Pb^{2+} ions from the solution to the adsorbent (Goyal *et al.*, 2021). By contrast, the adsorption efficiency decreased as the concentration of Pb^{2+} increased due to the competition among the overcrowded Pb^{2+} ions. At a lower concentration, the Pb^{2+} ions were readily adsorbed into the adsorbent. However, at higher concentrations, the adsorption rate was reduced due to intraparticle diffusion and competition among the crowded Pb^{2+} ions (Obike *et al.*, 2018).

Figure 10. Effect of the initial concentration of Pb^{2+} ions on adsorption efficiency and capacity

Adsorption Kinetics

To identify the adsorption rate and mechanism of Pb^{2+} in MIL-100(Fe)-EDTA, kinetic methods, including pseudo-first order and pseudo-second order, were investigated using time variations. The adsorption kinetic curves are presented in **Figure 11**, and the parameters are shown in Table 1.

Figure 11. Adsorption kinetic curves for pseudo-first order (a) and pseudo-second order (b) Pb^{2+} ions in MIL-100(Fe)-EDTA

Experimental data for metal ion adsorption were analyzed for the study of adsorption kinetics using pseudo-first order (3) and pseudo-second order (4) equations.

$$\text{Log } (q_e - q_t) = \text{log } q_e - \frac{k_1}{2,303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where q_e and q_t (mg/g) are the adsorption amount of Pb (II) on adsorbents at an equilibrium state and at the time of t (min); k_1 (1/min) and k_2 (g/(mg.min)) are rate constants of the pseudo-first-order and pseudo-second-order kinetics models.

Table 1. Adsorption kinetic model parameters of Pb^{2+} ions in MIL-100(Fe)-EDTA

Pseudo-first order kinetics			Pseudo-second order kinetics		
k (min ⁻¹)	q_e (mg/g)	R^2	k (g/mg.min)	q_e (mg/g)	R^2
0.0018	0.8999	0.7493	0.0109	3.1928	0.9981

The correlation coefficient, R^2 , for the pseudo-first order and pseudo-second order kinetics was 0.7493 and 0.9981, respectively (Table 1). Higher value in the later indicated that the adsorption kinetic followed a pseudo-second order. This kinetic model describes the adsorption rate as the function of adsorption capacity and suggests that the adsorption mechanism occurs via chemisorption, involving electron transfer between the adsorbates and adsorbents, or in this case, complexation of Pb^{2+} ions with MIL-100(Fe)-EDTA (Fang *et al.*, 2014). The low k_2 showed that the adsorption rate decreased with decreasing unoccupied sites number and increasing time (El-Sayed *et al.*, 2016).

A kinetic study by Forghani *et al.* (2020) demonstrated that Pb^{2+} ions adsorption by MIL-100(Fe) followed the pseudo-first order model with total capacity at equilibrium up to 10.53 mg/g that indicated weak physisorption (Tanzifi *et al.*, 2017). Compared to MIL-100(Fe), the adsorption efficiency in MIL-100(Fe)-EDTA was much higher due to the strong chelation between Pb^{2+} ions and EDTA.

Adsorption Isotherms

Experimental data were also analyzed using two-parameter isotherm models, Langmuir and Freundlich, to further investigate the interaction between Pb^{2+} and the adsorbent. The adsorption isotherm was calculated, and the results are described in Figure 12 and Table 2.

Figure 12. Adsorption isotherm of Pb^{2+} adsorbed onto MIL-100(Fe)-EDTA using Langmuir (a) and Freundlich (b) models

The equation model used to describe adsorption isotherm data is the Langmuir and Freundlich adsorption isotherm models. Equation (5) shows the Langmuir adsorption isotherm:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max}K_1C_e} \quad (5)$$

where q_e is the adsorption amount of Pb(II) on adsorbents (mg/g) at an equilibrium state, $q_{\max}$ is the adsorption capacity of metals on adsorbents (mg/g), C_e is the equilibrium concentration of metals (mg/g), and K_1 is the Langmuir adsorption constant related to adsorption energy. The Freundlich model is shown in Equation (6):

$$q_e = KfC_e^{1/n} \quad (6)$$

where q_e is the adsorption amount of Pb(II) on adsorbents (mg/g) at an equilibrium state, C_e is the equilibrium concentration of metals (mg/g), and K_f and n are Freundlich constants that are, respectively, related to adsorption capacity and adsorption intensity.

Table 2. Adsorption isotherm parameters calculated from Langmuir and Freundlich models

Langmuir				Freundlich		
K_L (L/mol)	R^2	E_{ads} (kJ/mol)	q_{maks} (mg/g)	K_f (mol/g)	N	R^2
248182.0664	0.9559	31.2926	7.5141	0.1759	2.1445	0.6996

Table 2 shows that Pb^{2+} ions adsorption using MIL-100(Fe)-EDTA corresponded to Langmuir model, as the calculated R^2 for Langmuir isotherm was higher than that of Freundlich. This model shows that the adsorption process occurred homogenously and generated monolayer

at the surface of MIL-100(Fe)-EDTA, since adsorption could not take place at the already occupied sites and covered surface (Huang *et al.*, 2015). The result also supports the kinetic study and proves that the interaction between Pb^{2+} ions and MIL-100(Fe)-EDTA is chemisorption.

Forghani *et al.* (2020) indicated that the adsorption isotherm of Pb^{2+} ions using MIL-100(Fe) followed the Langmuir model, with a maximum adsorption capacity of up to 22.86 mg/g. This suggests that the adsorption process of Pb^{2+} using both MIL-100(Fe) and MIL-100(Fe)-EDTA occurs at the surface of the material by chemically forming a monolayer with active sites (Kim *et al.*, 2015).

Conclusions

The electrochemical attachment of EDTA to MIL-100(Fe) significantly improved the capability of the material to adsorb Pb^{2+} ions. The adsorption followed a pseudo-second order kinetic model and Langmuir isotherm that showed that the adsorption occurred via chemisorption. Optimization studies revealed that the maximum adsorption was achieved in a solution with an initial Pb^{2+} concentration of 5 ppm at pH 3 with a contact time of 12 h. MIL-100(Fe)-EDTA exhibited high stability in the intestinal simulation medium (pH 1.2) as well as in the stomach simulation medium (pH 6), indicating that the material has considerable potential for use as a functional Pb^{2+} detoxification agent in human body. Further in vivo studies related to this study are currently in progress in our group.

Declarations

Ethics Approval

Not applicable

Consent to Participate

Not applicable

Consent for Publication

Not applicable

Availability of Data and Materials

Not applicable

Competing Interests

The authors declare that they have no competing interests

Funding

This research was funded by Universitas Sebelas Maret via PNBPN Research Grant in the scheme Advanced Applied Research (PUT) project number 260/UN27.22/HK.07.00/2021

Authors' Contributions

WWL conceptualized and supervised the research, wrote, revised also analyzed and interpreted the data. RM performed the synthesis of the material and the examination on Pb^{2+} adsorption, also wrote the draft. IN supervised the research and interpreted the data. LL wrote and revised the draft.

Acknowledgements

We would like to acknowledge Universitas Sebelas Maret for a PNBPN research grant in the scheme Advanced Applied Research (PUT) project number 260/UN27.22/HK.07.00/2021.

References

- Abednatanzi S, Abbasi A, Masteri-Farahani M (2017) Immobilization of catalytically active polyoxotungstate into ionic liquid-modified MIL-100(Fe): A recyclable catalyst for selective oxidation of benzyl alcohol. *Catal Commun.* 96:6-10. <https://doi.org/10.1016/j.catcom.2017.03.011>
- Akarmazyan SS, Panagiotopoulou P, Kambolis A, Papadopoulou C, Kondarides DI (2014) Methanol dehydration to dimethylether over Al_2O_3 catalysts. *Appl Catal B: Environ.* 145:136-148. <https://doi.org/10.1016/j.apcatb.2012.11.043>

- Bezverkhyy I, Weber G, Bellat J (2016) Degradation of fluoride-free MIL-100 (Fe) and MIL-53 (Fe) in water : Effect of temperature and pH. *Micropor Mesopor Mater.* 219:117-124. <https://doi.org/10.1016/j.micromeso.2015.07.037>
- El-Sayed M, Eshaq G, ElMetwally AE (2016) Adsorption of heavy metals from aqueous solutions by Mg-Al-Zn mingled oxides adsorbent. *Water Sci Technol.* 74:1644-1657. <https://doi.org/10.2166/wst.2016.329>
- Fang X, Zong B, Mao S (2018) Metal-organic framework-based sensors for environmental contaminant sensing. *Nano-Micro Lett.* 10:1-19. <https://doi.org/10.1007/s40820-018-0218-0>
- Feng L, Cao M, Ma X, Zhu Y, Hu C (2012) Superparamagnetic high-surface-area Fe₃O₄ nanoparticles as adsorbents for arsenic removal. *J. Hazar. Mater.* 217:439-446. <https://doi.org/10.1016/j.jhazmat.2012.03.073>
- Forghani M, Azizi A, Livani MJ, Kafshgari LA (2020) Adsorption of lead(II) and chromium(VI) from aqueous environment onto metal-organic framework MIL-100(Fe): Synthesis kinetics equilibrium and thermodynamics. *J. Solid State Chem.* 291:121636. <https://doi.org/10.1016/j.jssc.2020.121636>
- Goyal P, Tiwary CS, Misra SK (2021) Ion exchange based approach for rapid and selective Pb(II) removal using iron oxide decorated metal organic framework hybrid. *J. Environ Manage* 277:111469. <https://doi.org/10.1016/j.jenvman.2020.111469>
- Han L, Qi H, Zhang D, Ye G, Zhou W, Hou C, Sun Y (2017) A facile and green synthesis of MIL-100(Fe) with high-yield and its catalytic performance. *New J. Chem.* 41:13504-13509. <https://doi.org/10.1039/C7NJ02975F>
- Horcajada P, Surblé S, Serre C, Hong DY, Seo YK, Chang JS, Férey G (2007) Synthesis and catalytic properties of MIL-100(Fe) an iron(III) carboxylate with large pores. *Chem. Commun.* 100:2820-2822. <https://doi.org/10.1039/B704325B>
- Huang G, Wang D, Ma S, Chen J, Jiang L, Wang P (2015) A new low-cost adsorbent: Preparation characterization and adsorption behavior of Pb(II) and Cu(II). *J. Colloid Interf. Sci.* 445:294-302. <https://doi.org/10.1016/j.jcis.2014.12.099>

- Huang S, Yang KL, Liu XF, Pan H, Zhang H, Yang S (2017) MIL-100(Fe)-catalyzed efficient conversion of hexoses to lactic acid. *RSC Adv.* 7:5621-5627. <https://doi.org/10.1039/C6RA26469G>
- Huo SH, Yan XP (2012) Metal-organic framework MIL-100(Fe) for the adsorption of malachite green from aqueous solution. *J. Mater. Chem.* 22:7449-7455. <https://doi.org/10.1039/C2JM16513A>
- Jin HX, Xu HP, Wang N, Yang LY, Wang YG, Yu D, Ouyang XK (2019). Fabrication of carboxymethylcellulose/metal-organic framework beads for removal of Pb(II) from Aqueous Solution. *Materials* 12:942. <https://doi.org/10.3390/ma12060942>
- Kim PJ, You YW, Park H, Chang JS, Bae YS, Lee CH, Suh JK (2015) Separation of SF₆ from SF₆/N₂ mixture using metal-organic framework MIL-100 (Fe) granule. *Chem. Eng. J.* 262:683-690. <https://doi.org/10.1016/j.cej.2014.09.123>
- Klapiszewski Ł, Bartczak P, Wysokowski M, Jankowska M, Kabat K, Jesionowski T (2015) Silica conjugated with kraft lignin and its use as a novel “green” sorbent for hazardous metal ions removal. *Chem. Eng. J.* 260:684-693. <https://doi.org/10.1016/j.cej.2014.09.054>
- Lestari WW, Hartono J, Adreane M, Nugrahaningtyas KD, Purnawan C, Rahardjo SB (2016) Electro-synthetic optimization of host material Based on MIL-100 (Fe). *Molekul* 11:61-70. <http://dx.doi.org/10.20884/1.jm.2016.11.1.195>
- Lim TT, Chui PC, Goh KH (2005) Process evaluation for optimization of EDTA use and recovery for heavy metal removal from a contaminated soil. *Chemosphere* 58:1031-1040. <https://doi.org/10.1016/j.chemosphere.2004.09.046>
- Luo X, Ding L, Luo J (2015) Adsorptive removal of Pb(II) ions from aqueous samples with amino-functionalization of metal-organic frameworks MIL-101(Cr). *J Chem Eng Data* 60:1732-1743. <https://doi.org/10.1021/je501115m>
- Madadrang CJ, Kim HY, Gao G, Wang N, Zhu J, Feng H, Hou S (2012) Adsorption behavior of EDTA-graphene oxide for Pb (II) removal. *ACS Appl Mater Inter.* 4:1186-1193. <https://doi.org/10.1021/am201645g>
- Maiti S, Pramanik A, Manju U, Mahanty S (2015) Reversible lithium storage in manganese 1,3,5-Benzenetricarboxylate metal-organic framework with high capacity and rate performance. *ACS Appl. Mater. Inter.* 7:16357-16363. <https://doi.org/10.1021/acsami.5b03414>

500 Mobasherpour I, Heshajin MS, Kazemzadeh A, Zakeri M (2007) Synthesis of nanocrystalline
 501 hydroxyapatite by using precipitation method. *J. Alloy Compd.* 430:330-333.
 502 <https://doi.org/10.1016/j.jallcom.2006.05.018>
 503 Narayanan A, Dhamodharan R (2015) Super water-absorbing new material from chitosan EDTA
 504 and urea. *Carbohydr. Polym.* 134:337-343. <https://doi.org/10.1016/j.carbpol.2015.08.010>
 505 Nguyen DTC, Le HTN, Do TS, Pham VT, Tran DL, Ho VTT, Doan VT (2019) Metal-Organic
 506 Framework MIL-53(Fe) as an adsorbent for ibuprofen drug removal from aqueous
 507 solutions: Response surface modeling and optimization. *J. Chem.* 2019:1-11.
 508 <https://doi.org/10.1155/2019/5602957>
 509 Obike AI, Igwe JC, Emeruwa CN, Uwakwe KJ (2018) Equilibrium and kinetic studies of Cu (II)
 510 Cd (II) Pb (II) and Fe (II) adsorption from aqueous solution using cocoa (*Theobroma*
 511 *cacao*) pod husk. *J. Appl Sci Env Manage.* 22:182-190.
 512 <https://doi.org/10.4314/jasem.v22i2.5>
 513 Peng Y, Huang H, Zhang Y, Kang C, Chen S, Song L, Zhong C (2018) A versatile MOF-based
 514 trap for heavy metal ion capture and dispersion. *Nat. Commun.* 9:1-9.
 515 <https://doi.org/10.1038/s41467-017-02600-2>
 516 Rivera JM, Rincón S, Ben Youssef C, Zepeda A (2016) Highly efficient adsorption of aqueous
 517 Pb(II) with mesoporous metal-organic framework-5: An equilibrium and kinetic study. *J.*
 518 *Nanomater.* 2016:1-9. <https://doi.org/10.1155/2016/8095737>
 519 Rojas S, Baati T, Njim L, Manchego L, Neffati F, Abdeljelil N, Horcajada P (2018) Metal-organic
 520 frameworks as efficient oral detoxifying agents. *J. Am Chem Soc.* 140:9581-9586.
 521 <https://doi.org/10.1021/jacs.8b04435>
 522 Saleh TA, Sari A, Tuzen M (2017) Optimization of parameters with experimental design for the
 523 adsorption of mercury using polyethylenimine modified-activated carbon. *J. Env. Chem.*
 524 *Eng.* 5:1079-1088. <https://doi.org/10.1016/j.jece.2017.01.032>
 525 Seo YK, Yoon JW, Lee JS, Lee UH, Hwang YK, Jun CH, Chang JS (2012) Large scale fluorine-
 526 free synthesis of hierarchically porous iron(III) trimesate MIL-100(Fe) with a zeolite MTN
 527 topology. *Micropor Mesopor Mater.* 157:137-145.
 528 <https://doi.org/10.1016/j.micromeso.2012.02.027>

529 Shi J, Hei S, Liu H, Fu Y, Zhang F, Zhong Y, Zhu W (2013) Synthesis of MIL-100(Fe) at low
 530 temperature and atmospheric pressure. *J. Chem.* 2013:1-4.
 531 <https://doi.org/10.1155/2013/792827>

532 Sun DT, Peng L, Reeder WS, Moosavi SM, Tiana D, Britt DK, Queen WL (2018) Rapid selective
 533 heavy metal removal from water by a metal-organic framework/polydopamine composite.
 534 *ACS Central Sci.* 4:349-356. <https://doi.org/10.1021/acscentsci.7b00605>

535 Tanzifi M, Hosseini SH, Kiadehi AD, Olazar M, Karimipour K, Rezaiemehr R, Ali I (2017)
 536 Artificial neural network optimization for methyl orange adsorption onto polyaniline nano-
 537 adsorbent: Kinetic isotherm and thermodynamic studies. *J. Mol. Liq.* 244:189-200.
 538 <https://doi.org/10.1016/j.molliq.2017.08.122>

539 Wang B, Lv XL, Feng D, Xie LH, Zhang J, Li M, Zhou HC (2016) Highly stable Zr(IV)-based
 540 metal-organic frameworks for the detection and removal of antibiotics and organic
 541 explosives in water. *J. Am. Chem. Soc.* 138:6204-6216.
 542 <https://doi.org/10.1021/jacs.6b01663>

543 Wu J, Zhou J, Zhang S, Alsaedi A, Hayat T, Li J, Song Y (2019) Efficient removal of metal
 544 contaminants by EDTA modified MOF from aqueous solutions. *J. Colloid Interf. Sci.*
 545 555:403-412. <https://doi.org/10.1016/j.jcis.2019.07.108>

546 Yuan B, Wang X, Zhou X, Xiao J, Li Z (2019) Novel room-temperature synthesis of MIL-100(Fe)
 547 and its excellent adsorption performances for separation of light hydrocarbons. *Chem. Eng.*
 548 *J.* 355:679-686. <https://doi.org/10.1016/j.ccej.2018.08.201>

549 Zhang H, Wen J, Fang Y, Zhang S, Zeng G (2019) Influence of fulvic acid on Pb(II)removal from
 550 water using a post-synthetically modified MIL-100(Fe). *J. Colloid Interf. Sci.* 551:155-
 551 163. <https://doi.org/10.1016/j.jcis.2019.05.016>

552 Zhang K, Dai Z, Zhang W, Gao Q, Dai Y, Xia F, Zhang X (2021) EDTA-based adsorbents for the
 553 removal of metal ions in wastewater. *Coordin. Chem. Rev.* 434:213809.
 554 <https://doi.org/10.1016/j.ccr.2021.213809>

555 Zhou J, Liu Y, Zhou X, Ren J, Zhong C (2018) Magnetic multi-porous bio-adsorbent modified
 556 with amino siloxane for fast removal of Pb(II) from aqueous solution. *Appl. Surf. Sci.*
 557 427:976-985. <https://doi.org/10.1016/j.apsusc.2017.08.110>

558 Zhu H, Yuan J, Tan X, Zhang W, Fang M, Wang X (2019) Efficient removal of Pb 2^+ by Tb-
559 MOFs: identifying the adsorption mechanism through experimental and theoretical
560 investigations. *Env. Sci.: Nano.* 6:261-272. <https://doi.org/10.1039/C8EN01066H>

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [ElectronicSupportingInformation10082021.docx](#)