

Conversion of the styrofoam waste into a high-capacity and recoverable adsorbent in the removing the toxic Pb^{2+} from water media

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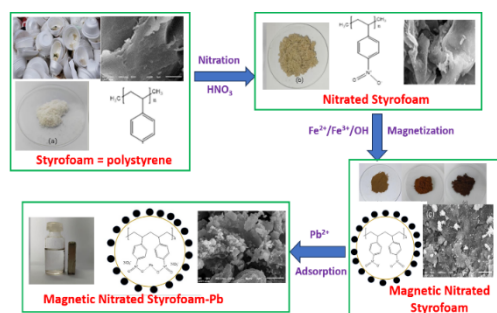
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Graphical abstract



Abstract

The sequential nitration and magnetization of waste styrofoam to form a novel adsorbent has been investigated. The novelty of this study assigned approach lies in the introduction of an anionic surface on the styrofoam, enabling it to adsorb cationic Pb^{2+} ion, combined with its magnetic property that facilitates rapid and practical recovery. The nitration was conducted using concentrated nitric acid in the presence of sulfuric acid, and the magnetization was performed by coprecipitation of Fe^{2+} and Fe^{3+} at high pH to form Fe_3O_4 . The prepared adsorbents were characterized using Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), and Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) instruments. The characterization data clearly showed the evidence that nitrated-magnetic-styrofoam was successfully produced. The adsorption process of Pb^{2+} ion from aqueous media was evaluated via batch experiment. The contact time of the adsorption, adsorbent weight, solution pH, and initial concentration of Pb^{2+} were optimized to get the best adsorption condition. The adsorbent with 33.3 wt% of Fe_3O_4 fraction revealed a compromise of high adsorption effectivity around 90.0% and efficient separability with the optimum condition of 30 mg adsorbent dose at solution pH 6 within 60 minutes of adsorption time and initial concentration at $50 \text{ mg L}^{-1} \text{ Pb}^{2+}$. The parameters isotherm and kinetic of adsorptions were also determined. According to three simulated isotherm

models of Langmuir, Freundlich, and Sips, Langmuir isotherm is well-fitted with an adsorption capacity of 9.81 mg g^{-1} . The adsorption kinetic matches to a pseudo-second order giving an adsorption rate constant of $0.131 \text{ g mg}^{-1} \text{ min}^{-1}$ and is expected to give chemisorption mechanism.

Keywords: Styrofoam, magnetic, nitration, adsorption, Pb^{2+} , removal

1. Introduction

In the last decade, waste styrofoam has been found abundantly in the environment originating from the large disposal of styrofoam cups, food trays, and electronic goods (Mahmoud *et al.* 2016; Milla *et al.* 2018; Omapas *et al.* 2015; Siyal *et al.* 2012 (Sihombing *et al.* 2022). Styrofoam is composed by almost 5% of polystyrene and the left is 95%, giving its high lightweight (Kol *et al.* 2023; Bekri-Abbes *et al.* 2006). Waste styrofoam has characteristics such as very stable chemical properties, aging resistance, and non-degradability. This white solid waste is recognized as a global environmental threat and waste management problem (Mohammed and Rao 2023; Mahmoud *et al.* 2016). Chronic polystyrene, as the main component in styrofoam, contaminating human body is reported to show adversely affects on the central nervous system, manifesting symptoms such as depression, headache, fatigue, and weakness (Milla *et al.* 2018; Omapas *et al.* 2015). The minor effects on kidney function and blood created by polystyrene is also notified (Bekri-Abbes *et al.* 2006; Mahmoud *et al.* 2016; Milla *et al.* 2018; Omapas *et al.* 2015; Siyal *et al.* 2012).

Recently, the conversion of waste styrofoam into a sulfonated adsorbent has been intensively developed, which could change the hydrophobic surface into a negative hydrophilic surface (Bekri-Abbes *et al.* 2006; Mahmoud *et al.* 2016; Milla *et al.* 2018; Omapas *et al.* 2015; Siyal *et al.* 2012). This negatively charged styrofoam adsorbent has garnered significant attention and has been investigated for reducing the concentrations of various cationic heavy toxic metals, such as Cd (II) (Bekri-Abbes *et*

al. 2006; Milla *et al.* 2018; Omapas *et al.* 2015; Tran *et al.* 2023), Hg(II) (Mahmoud *et al.* 2016), and Pb(II) (Bekri-Abbes *et al.* 2006; Mahmoud *et al.* 2016; Soliman *et al.* 2016). In addition to sulfonation, there has also been considerable interest in nitration to transform the waste styrofoam into a negatively charged adsorbent. Comparative results have shown that nitrated styrofoam exhibits a higher adsorption capacity than its sulfonated alternative (Tran *et al.* 2023; Mahmoud *et al.* 2016). However, there is a lack of reports on the nitration of styrofoam to remove certain toxic metal ions, which encourages us to further explore this area.

In general, at the end of the adsorption process, recovery of the spent adsorbent through filtration is inconvenient and expensive, especially for large-scale applications. Consequently, significant efforts have been directed toward replacing this impractical separation method by modifying it with Fe₃O₄ to create a magnetic adsorbent that can be easily separated and recovered (Al-Sabagh *et al.* 2018; Mohseni-Bandpi *et al.* 2016; Mtshatsheni *et al.* 2019; Pambudi *et al.* 2020; Wahyuni *et al.* 2022). In recent years, magnetic adsorbents have attracted much interest because they not only have high separation efficiency and reusability but also have a large adsorption capacity for contaminant removal. The magnetic adsorbents developed include natural zeolite (Pambudi *et al.* 2020), activated carbon (Mtshatsheni *et al.* 2019), polystyrene synthetic (Al-Sabagh *et al.* 2018), and sulfonated waste styrofoam (Wahyuni *et al.* 2022). To the best of our knowledge, the magnetization of nitrated waste styrofoam adsorbent has not been explored.

In the current study, the sequential nitration and magnetization of Styrofoam waste are systematically explored to create an affordable, efficient, and recoverable adsorbent for the removal of Pb²⁺ ions. Removal of Pb²⁺ from water media or industrial wastewater is essential since Pb²⁺ is the heavy metal ion contaminating water can create some adverse effects both for human health and the environment that can accumulate in the food chain even in the small concentration (Biswal and Balasubramanian 2023; Hemavathi *et al.* 2023). Exposure to Pb in human damages to the nervous system, liver, reproductive system, and kidneys, as well as causing cancer, anemia, kidney disease, IQ decreasing of children, mental retardation (Wang *et al.* 2024; Ghorbani *et al.* 2020). In water, Pb²⁺ is hazard for biotics as well as for probiotic microbes and could not biodegrade, thereafter leads to the environmental damaged (Huda *et al.* 2023; Zhu *et al.* 2023). In the present research, in order to obtain the highest Pb²⁺ adsorption, several conditions including contact time, adsorbent mass, solution pH, and initial Pb²⁺ concentration, are optimized. and kinetic parameters are also determined. Thereafter, this study is expected to fabricate the functional material from waste management of polystyrene modified by nitration and magnetization in order enhance their performance in the removal of the heavy metal of Pb²⁺ contaminant effectively.

2. Materials and methods

2.1. Chemicals

The chemicals used in this study are Nitric acid, Fe (NH₄) (SO₄)₂, Fe (NO₃)₃, Pb (NO₃)₂, NH₄OH, NaCl and HCl. All chemicals purchased from Merck Co Inc (Germany) and were used without any purification.

2.2. Characterization instruments

Instruments operated in this research were Frontier Transform-Infra Red (FTIR) Shimadzu IR Prestige-21 to record the existing functional group in the adsorbent materials, Shimadzu 6000X X-ray diffractometer (XRD) equipped with Cu- K α radiation to characterize the crystallinity of adsorbents materials, Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX) to observe the surface morphology of adsorbents material after nitration and magnetization, and LaMotte 2020 (17999-EX2) turbidimeter were used to investigate the turbidity of wastewater after adsorption process by using the magnetization adsorbents. In addition, atomic absorption spectrophotometer (AAS) Thermo Scientific iCE 3000 was also operated for measuring the remaining concentration of Pb²⁺ after adsorption process.

2.3. Procedures

2.3.1. Nitration process of styrofoam

The nitration procedure was conducted following the procedure reported previously (Mahmoud *et al.* 2016). For this typical process, 3 grams of the styrofoam waste powder having 60 mesh was added into 50 mL of a solution containing concentrated HNO₃ and H₂SO₄ acid with a ratio volume of 40:10 mL. The mixture of styrofoam powder with the acids was stirred magnetically for 24 h at room temperature. After the desired time, the nitrated styrofoam was separated from the acid solution by filtration, that was continued by washing with distilled water to get pH 6, and then was washed with ethanol 96%. Then the washed nitrated Styrofoam was dried at 60-70 °C for 5 h and the dry adsorbent obtained was noted as sty-NO₂.

2.3.2. Magnetization of sty-NO₂

The magnetization of the sty-NO₂ adsorbent with Fe₃O₄ was performed by the co-precipitation of Fe²⁺- Fe³⁺ in the basic media (Sun *et al.* 2023; Koo *et al.* 2019; Petcharoen and Sirivat, 2012). About 1.5 g of sty- NO₂ was suspended in 400 mL of the NH₄OH 0.5 mole L⁻¹ solution. Then, the suspension was heated at 70 °C for 30 min. At the same time, it was added drop-wise with a 100 mL solution containing Fe²⁺ and Fe³⁺ with the mole ratio of 1:2, under nitrogen gas, and stirred for about 15 minutes until the black solid was produced. Then, the black solid was separated from the filtrate by contacting a magnet rod onto the outside wall of the flask. The recovered adsorbent was rinsed with deionized water up to neutral pH and dried at 70°C for 2 h. The black solid was ground and sieved to get a 200-mesh powder. The black powder was notified as sty-NO₂ /Fe₃O₄ with 50 wt% of the Fe₃O₄ fraction. The same procedure was duplicated for sty-NO₂ as weight 3.0 g and 4.5 g to obtain sty-NO₂ /Fe₃O₄ with 33.3 wt% and 25.0 wt%

of Fe₃O₄ fractions, respectively. All adsorbents obtained were notified as sty-NO₂/Fe₃O₄ (25), sty-NO₂/Fe₃O₄ (33.3), and sty-NO₂/Fe₃O₄ (50), following the fractions of Fe₃O₄.

2.3.3. Characterization of sty-NO₂/Fe₃O₄ adsorbents

The FTIR spectra of KBr palleted samples were recorded from 400-4000 cm⁻¹ of the wavenumber, XRD patterns were scanned from 10-90° of the diffractions angles, and the SEM-EDX images were taken with 1000-5000× magnification. The separable effectiveness of sty-NO₂/Fe₃O₄ adsorbents represented by turbidity, was measured by a turbidimeter. The adsorption capacity of the adsorbents was examined for Pb²⁺ adsorption. The Fe₃O₄ fraction that gave the best separability and adsorption capacity can be found from the separation and adsorption studies. Thus, each mode of Fe₃O₄ fraction in sty-NO₂ adsorbent were used in adsorption experiment for gaining the optimum fraction of Fe₃O₄ attached in sty-NO₂ adsorbent. The best adsorbent then was employed for Pb²⁺ adsorption by altering contact time, adsorbent weight, initial Pb²⁺ concentration, and solution pH also used as a representative adsorbent for compositional and morphological characterization compared with the pristine sample and unmagnetized sty-NO₂ adsorbent.

2.3.4. Adsorption process

In the adsorption process, a beaker glass filled with 50 mL of Pb²⁺ solution 10 ppm at pH 5 was added with 30 mg of sty-NO₂/Fe₃O₄ (the best ratio) along with stirring for 1 h. After that, sty-NO₂/Fe₃O₄ adsorbent was separated by contacting the magnetic rod into the outer wall of the beaker glass. Then the absorbance of the solution from the adsorption was measured by AAS instrument, to determine the concentration of Pb²⁺ left in the solution that was not adsorbed.

The percentage of Pb²⁺ was calculated referring to the difference among the initial (C_i) and equilibrium (C_e) concentrations of pollutants in the liquid phase after the separation using following equations (Eq 1-2) (Li *et al.* 2024):

$$\text{Adsorption (\%)} = \frac{C_i - C_e}{C_i} \times 100\% \quad (1)$$

$$Q_e = \frac{v(C_i - C_e)}{W} \quad (2)$$

Where C_i and C_e are the initial and equilibrium of metal ions concentration. Q_e are equilibrium adsorption capacity. W is the adsorbent weight (mg) and v is the volume of metal ion solution (L).

As the adsorption process is conducted in batch technique, the same procedure abovementioned was also copied for other adsorption parameters to obtain the optimum adsorption condition. The optimum pH gained from first batch was used in the experiment to find the optimum adsorption time, following by adsorption weight and Pb²⁺ initial concentration. The data obtained would be used to determine the kinetics model and isotherm adsorption.

The experiment for obtaining optimum adsorption time and initial concentration of Pb²⁺ was simulated in kinetics

model pseudo first order and pseudo second order according to the equations below (Eq 3-4), respectively (Gautam *et al.* 2023; Wang *et al.* 2024) :

$$\ln(q_e - q_t) = \ln q_e - (k_1 \times t) \quad (3)$$

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

Where k₁ (min⁻¹) is the pseudo-first order rate constants, k₂ (g mmol min⁻¹) is the pseudo-second ordered, q_t is amount of Pb²⁺ in certain time (mmol g⁻¹), q_e denotes amount of Pb²⁺ at equilibrium state (mmol g⁻¹), and t is the adsorption time (min).

Meanwhile for study the isotherm adsorption, several models are used in this research (Eq 5-8) (Gautam *et al.* 2023; Chukwu Onu *et al.* 2023):

1. Langmuir

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

q_e and C_e for all equation denoted as the amount of (mg g⁻¹) and concentration (mg L⁻¹) of Pb²⁺ adsorbed at equilibrium, K_L is the Langmuir constant corresponding to the rate of adsorption and adsorption capacity.

2. Freundlich

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

K_F is the Freundlich constant and n is attributed to adsorption intensity and heterogeneity factor which shows the deviation in adsorption linearity and is a function of adsorption capacity.

3. Sips

$$q_e = \frac{q_m (K_S C_e)^m}{1 + (K_S C_e)^m} \quad (7)$$

K_S is Sips isotherm constant relating to the adsorption energy known as adsorption affinity. Meanwhile q_m for all equations assigned to maximum adsorption capacity (mg g⁻¹), and m is denoted to exponent for Sips isotherm equation

4. Toth

$$q_e = \frac{q_m K_T C_e}{(1 + (K_T C_e)^t)^{1/t}} \quad (8)$$

K_T stands for Toth isotherm constant relating to adsorption energy known as adsorption affinity. Whereas, t is exponent for Toth isotherm model assigned to the heterogeneity factor.

For all isotherm models are analyzed and validated based on R² values via non-linear regression analysis and standard deviation.

3. Results and discussion

3.1. Preparation of the magnetic nitrated styrofoam adsorbent

The nitrated styrofoam adsorbent is formed through the substitution of hydrogen atom of styrene by nitro group from nitrate acid catalyzed by sulfuric acid (Mahmoud *et al.*

2016; Omapas *et al.* 2015). This nitration resulted in the negative surface of styrofoam, and the reaction is exhibited in Figure 1.

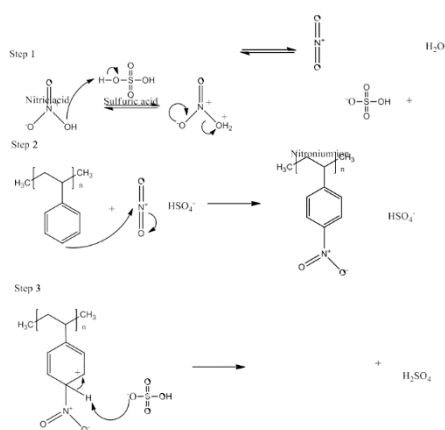
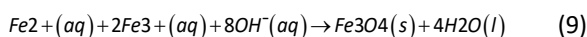


Figure 1. Reactions occurred during the nitration of styrofoam in the present sulfuric acid as a catalyst

Then, Fe_3O_4 contributing magnetic property toward the nitrated styrofoam adsorbent is produced via coprecipitation of a mixture of Fe^{2+} and Fe^{3+} in the presence of a basic solution of NH_4OH (Sun *et al.* 2023). The reaction is depicted as (Eq 9), where the Fe_3O_4 may be formed on the surface of the nitrated styrofoam.



4. Characterization result

4.1. FTIR spectra

The respective spectra are exhibited in Figure 2. In the spectra of styrofoam, several peaks at the wavenumbers of 3024, 2924, 1604, and 694 cm^{-1} can be noticed. Peaks at 3204 cm^{-1} refers to the C-sp stretching, at 2924 cm^{-1} may be associated with C-sp³ stretching asymmetric, at 2846 cm^{-1} should represent C-sp³ stretching symmetric, at 1604 cm^{-1} indicates the presence of C=C benzene aromatic ring, and at 694 cm^{-1} can be from C-H out of plane benzene ring (Tarek Ghaly *et al.* 2023; Liu *et al.* 2021; Yu *et al.* 2017). The

Table 1. FTIR absorption bands details for adsorbent samples

No	Samples	Wavenumber (cm^{-1})	Type of bonds
1.	Styrofoam	3204	C-sp stretching
		2924	C-sp ³ stretching asymmetric
		2846	C-sp ³ stretching symmetric
		1604	C=C benzene aromatic ring
		694	C-H out of plane benzene ring
2.	Sty-NO ₂ All bands in Styrofoam were found with additional bands	856	C-N stretching
		1519	N-O stretching asymmetric
		1350	N-O stretching symmetric
3.	Sty-NO ₂ /Fe ₃ O ₄ All bands in Sty-NO ₂ were found with additional band	586	Fe-O stretching
			According to the reference of Fe ₃ O ₄ absorption bands.

4.2. XRD patterns

The XRD patterns of all adsorbents are depicted in Figure 3. It is demonstrated that both styrofoam waste and sty-NO₂ exhibit featureless patterns, indicating that these adsorbents are in the amorphous phase. Such patterns of

bands observed confirm the chemical bonds and functional groups in the polystyrene, as a prominent component of styrofoam (Yu *et al.* 2017).

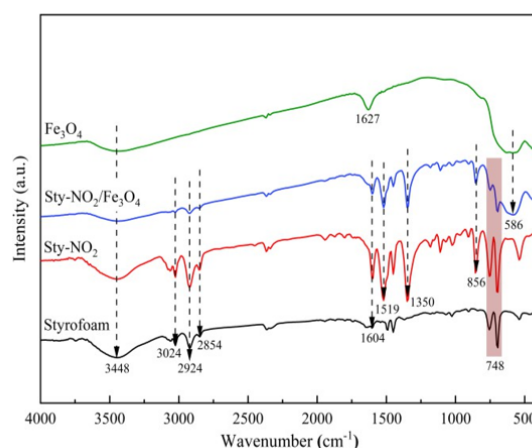


Figure 2 FTIR spectra of (a) Styrofoam, (b) Sty-NO₂, (c) Sty-NO₂/Fe₃O₄, (d) Fe₃O₄

Furthermore, the bands appearing in the spectra of styrofoam are also observable in the spectra of sty-NO₂, implying that the chemical structure of styrofoam is not influenced by the nitration process. In addition, some additional peaks at the wavenumbers of 856, 1519, and 1350 cm^{-1} are notified in the spectra of sty-NO₂. The wavenumbers are associated with stretching C-N, stretching N-O asymmetric and stretching N-O symmetric bonds, respectively (Deepika and Jagadeeshbabu, 2021; Mahmoud *et al.* 2016; Wang *et al.* 2013). The new bands confirm that nitration into styrofoam has successfully occurred. Moreover, in the spectra of sty-NO₂/Fe₃O₄, it is observed all bands belonged to sty-NO₂, with the new bands seen at 586 cm^{-1} . This new band is also observed in the spectra of Fe₃O₄ associated with Fe-O bond (Sun *et al.* 2023; Chang *et al.* 2016; Phadtare *et al.* 2019). Hence, it is strongly notified that sty-NO₂ has been obviously magnetized to form sty-NO₂/Fe₃O₄ adsorbent.

styrofoam and modified styrofoam have also been previously reported (Sihombing *et al.* 2022; Al- Sabagh *et al.* 2018; Xiao *et al.* 2017). The crystalline patterns belong to sty-NO₂/Fe₃O₄ and Fe₃O₄ which are clearly observable. XRD analysis of these materials reveals the presence of

peaks at 2θ : 30.03°, 35.28°, 42.90°, 53.75°, 57.04°, and 62.56° in accordance with JCPDS reference number 79-0418 (Sun *et al.* 2023; Abdullah *et al.* 2021; Al-Sabagh *et al.* 2018; Asab *et al.* 2020). Therefore, it can be inferred that iron oxide magnetic formed on the nitrated styrofoam must exist as Fe_3O_4 (magnetite), known for its high magnetic properties.

4.2.1. SEM images

The SEM images of styrofoam-based adsorbents are displayed in Figure 4. Styrofoam is illustrated as smooth sheets, whereas nitrated styrofoam appears as torn sheets. It is implied that nitration with concentrate nitric acid caused distortion in the styrofoam structure. Moreover, sty- $\text{NO}_2/\text{Fe}_3\text{O}_4$ is represented by torn sheets with some particles covering the surface of the sheet. The appearance of these particles closely resembles those of pure Fe_3O_4 ,

confirming the formation of Fe_3O_4 on the sty- NO_2 to form sty- $\text{NO}_2/\text{Fe}_3\text{O}_4$.

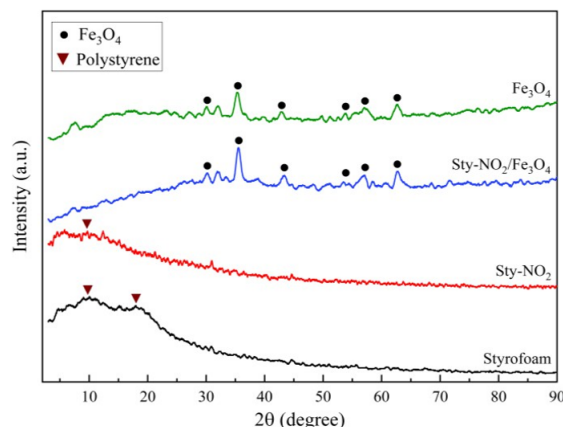


Figure 3. XRD patterns of (a) Styrofoam, (b) Sty- NO_2 , (c) Sty- $\text{NO}_2/\text{Fe}_3\text{O}_4$, (d) Fe_3O_4

Table 2. Diffractogram details of adsorbent samples

No	Samples	2θ identified	Type/Information
1.	Styrofoam	-	Amorphous/styrofoam
2.	Sty- NO_2	-	Amorphous/styrofoam
3.	Sty- $\text{NO}_2/\text{Fe}_3\text{O}_4$	30.03°, 35.28°, 42.90°, 53.75°, 57.04°, and 62.56°	Crystalline/ Fe_3O_4 based on the reference pattern of Fe_3O_4 JCPDS reference number 79-0418

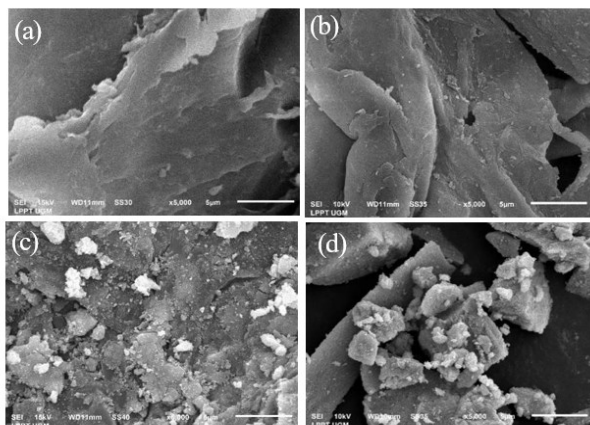


Figure 4 SEM images of (a) Styrofoam, (b) Sty- NO_2 , (c) Sty- $\text{NO}_2/\text{Fe}_3\text{O}_4$, and (d) Fe_3O_4

4.3. Adsorption results

4.3.1. Effect of Fe_3O_4 on the adsorption capacity

The presence of magnetite is hoped to contribute to the magnetic property of sty- NO_2 adsorbent, allowing the adsorbent to be easily and faster separated. In addition, Fe_3O_4 also provides negative charges that may be able to act as adsorption sites. Hence in Table 1, the Pb^{2+} adsorption resulted from various styrofoam-based adsorbents were presented. The styrofoam was able to adsorb Pb^{2+} but with very low effectiveness. Since styrofoam has hydrophobic properties, it inhibits from interacting with the polar or hydrophilic Pb^{2+} ion. Accordingly, the most possible reason is that Pb^{2+} ions may be only trapped in the polymer sheets of the styrofoam. The presence of Fe_3O_4 in the adsorbent could increase the

adsorption (Abadi *et al.* 2022; Mohseni-Bandpi *et al.* 2016) and the adsorption was continued to increase as the ascending fraction of Fe_3O_4 , but a further higher fraction led to a decrease in the adsorption. It is clearly implied that Fe_3O_4 provided active sites for Pb^{2+} adsorption. However, with the higher fraction of Fe_3O_4 in the adsorbent, Fe_3O_4 particles could form an aggregate with a larger size, which further provided a smaller surface area. As a consequent of the smaller surface area is the low adsorption.

With respect to the magnetic separability of the adsorbent, from Table 1, it can be seen that increasing Fe_3O_4 fraction resulted in a more effective separation as indicated by decreasing turbidity. It is important to note that, the higher turbidity represents that the solution is more turbid due to more colloidal content. The effective separation is notified by the cleaner solution, as seen in Figure 5, or by the lower turbidity.

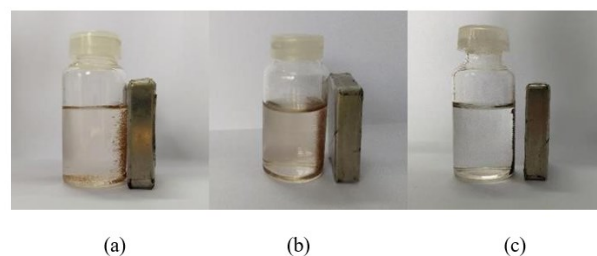


Figure 5. The appearance of the clearness of the solution separated from adsorbent of a) Sty- $\text{NO}_2/\text{Fe}_3\text{O}_4$ (25), b) Sty- $\text{NO}_2/\text{Fe}_3\text{O}_4$ (33.3), and c) Sty- $\text{NO}_2/\text{Fe}_3\text{O}_4$ (50)

Hence, by compromising the adsorption and separability effectiveness, sty- $\text{NO}_2/\text{Fe}_3\text{O}_4$ (33.3) can be selected as the

best adsorbent. For the further adsorption study, only sty-NO₂/Fe₃O₄ (33.3) was utilized.

Table 3. The effect of the Fe₃O₄ presence on the adsorption and separation effectiveness

Adsorbent	Adsorption effectiveness (%)	Turbidity (AU)
Sty-NO ₂ /Fe ₃ O ₄ (25)	87.24	45
Sty-NO ₂ /Fe ₃ O ₄ (33.3)	90.13	19
Sty-NO ₂ /Fe ₃ O ₄ (50)	85.08	10
Sty-NO ₂	80.35	-
Styrofoam	5	-

4.3.2. Influence of the contact time

Figure 6 depicts the quantity of the Pb²⁺ adsorbed on sty-NO₂ and on sty-NO₂/Fe₃O₄ during various times. It is observed that the extension time up to 30 minutes, the adsorption drastically increased, and the increase was slower when the time was prolonged from 30 to 60 minutes. The contact time longer than 60 mins had no effect on the adsorption.

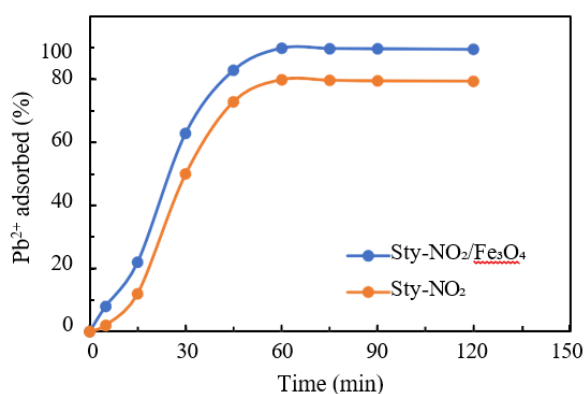


Figure 6. Influence of the contact time

In the beginning of the adsorption process, the adsorbent surface was still clean allowing effective adsorption. In a longer time, a lot of Pb²⁺ has been adsorbed and covered a larger part of the adsorbent surface, reducing the effectiveness of the adsorption. Hence the optimum adsorption time was 60 minutes, therefore the adsorption was not dependent on the contact time that longer than 60 minutes.

4.3.3. Influence of the solution pH

The adsorption effectiveness resulting from the process with alteration solution pH was presented in Figure 7. The increasing pH is seen to enhance the adsorption efficiency, and the adsorption reached maximum result at pH 6. The opposite adsorption effectiveness is observable as the pH was further increased.

At very low pH levels, a very large number of H⁺ was provided, which could interact with the nitro group (–NO₂) on the adsorbent's surface, resulting in a positive (protonated) charge. In such a solution pH, the Pb²⁺ ion should have existed maximally. However, under these conditions, the interaction between the adsorbate and the adsorbent surface was hindered due to repulsive forces, leading to inefficient adsorption. Increasing pH to 6 reduced the concentration of H⁺ ions while still allowing for

the potential protonation of the –NO₂ group on the surface of adsorbent, resulting in a neutralized surface charge. In such conditions, a large amount of Pb²⁺ ions may be found (Ahmad *et al.* 2019; Lin *et al.* 2021; Yao *et al.* 2016). This condition allowed the more effective adsorption.

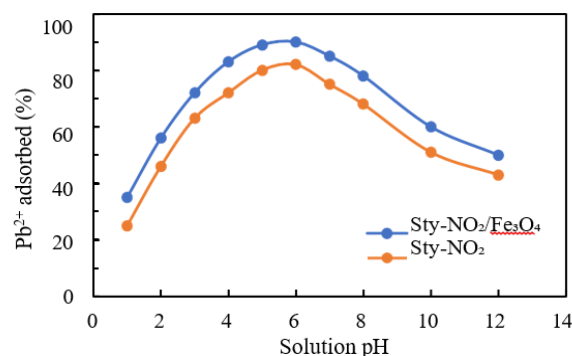


Figure 7. Influence of the solution pH

In the solution with pH 6, a smaller number of H⁺ ions were formed, preventing the protonation of the –NO₂ group, and a large number of Pb²⁺ ions were available, that was conducive for adsorption. This explains that the highest adsorption was reached at pH 6. As the solution pH was raised from 6 to 12, the amount of OH[–] ions increased and reacted with Pb²⁺ to form insoluble Pb(OH)₂, where the –NO₂ group was maximally formed (Hosseini-Bandegharaei *et al.* 2016; Wang *et al.* 2013).

Obviously, in such a situation, effective adsorption must be prohibited, and consequently, the adsorption was dismissed.

4.3.4. Influence of the adsorbent weight

As seen in Figure 8, the enlargement of the adsorbent weight could enhance the adsorption of Pb²⁺ which achieved the highest effectiveness when 30 mg adsorbent was utilized. The adsorbent higher than the optimum level did not change the adsorption results. The larger amount of the adsorbent, the more active adsorption sites could be provided, promoting more effective adsorption. The adsorption remained constant although the adsorbent weight was increased since the adsorption has already reached the equilibrium level.

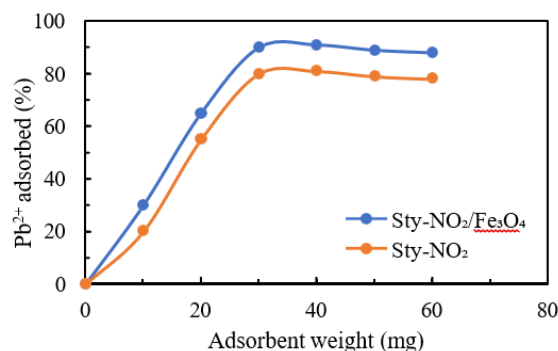


Figure 8. Influence of the adsorbent weight

4.3.5. Influence of the Pb²⁺ initial concentration

The influence of the Pb²⁺ initial concentration on the adsorption results is displayed in Figure 9. It was observed that the adsorption sharply increased when the initial

concentration was elevated up to 50 mg L^{-1} , but only slight improvements were noticeable for higher initial concentrations. At low concentrations with fewer Pb^{2+} ions, they could easily interact with the active sites on the adsorbent surface, and further promote effective adsorption. With higher concentration, more Pb^{2+} were present which made the solution more viscous and inhibited them from moving closer to the adsorbent. The summarized optimum condition from adsorption batch experiment of Pb^{2+} using the best adsorbent ratio of sty- $\text{NO}_2/\text{Fe}_3\text{O}_4$ (33.3) shown in Table 2.

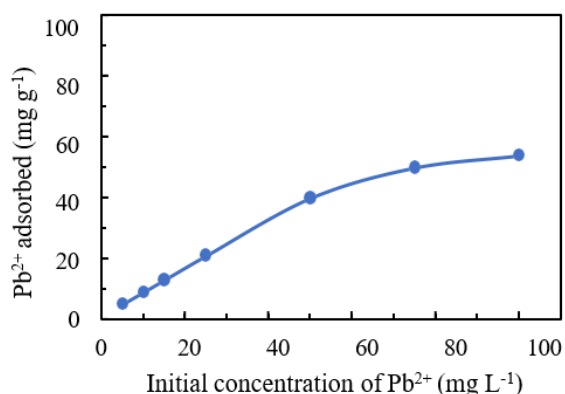


Figure 9. Influence of the Pb^{2+} initial concentration

Table 4. The optimum condition of adsorption parameter

No	Adsorption parameter	Optimum value
1.	Contact time	60 minutes
2.	pH	6
3.	Adsorbent weight	30 mg
4.	Adsorbate initial concentration	50 mg L^{-1}

4.3.6. Adsorption kinetic and isotherm

The understanding adsorption kinetics is essential before examining the adsorption mechanism through the isotherm model. In the initial step of the adsorption, the rapid uptake can be ascribed to the ample availability of unoccupied active sites on the adsorbent surface, increasing the adsorbate removal percentage. However, as the adsorption proceeds, repulsive forces between the metal ions attached to the adsorbent surface and those present in the liquid phase enhances the considerable diffusion resistance, which leads to a reduction in the adsorption rate over time. Hence, before the reduction of adsorption percentage occurs, we may obtain the optimum adsorption time and saturated concentration of adsorbate in contact with adsorbent.

Based on the calculation in the general equation of kinetics model used for heavy metal adsorption, the kinetic following first and second-orders were presented in Figure 10a and 10b, respectively and the kinetic parameters were summarized in Table 3. It is obviously seen that the pseudo-first-order curve shows less straight-line giving a linearity factor of 0.779, while the pseudo-second-order exhibits a good straight line with a 0.999 linearity factor. Therefore, it can be concluded that the rate of the Pb^{2+} adsorption by sty- $\text{NO}_2/\text{Fe}_3\text{O}_4$ adsorbent was controlled by both Pb^{2+} and

sty- $\text{NO}_2/\text{Fe}_3\text{O}_4$ as the assumption model of pseudo-second order. This model depicts that the valence bond forces encompassing mechanisms such as electron sharing, electron transfer, and ion exchange are likely implicated in the interaction between the adsorbents and the metal ions. Consequently, it can be deduced that the adsorption process of Pb^{2+} with sty- $\text{NO}_2/\text{Fe}_3\text{O}_4$ adsorbent governed by chemisorption (Li *et al.* 2024). This assumption would be supported the following study.

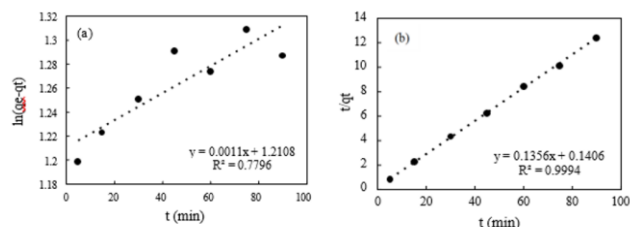


Figure 10. Kinetic study by following: (a) pseudo-first-order and (b) pseudo-second-order

Furthermore, the adsorption isotherm curves based on Freundlich and Langmuir models are displayed in Figure 11. From the figure, it appears that the linear straight line is shown by Langmuir curve, confirming that the adsorption well agreed with the Langmuir model. Langmuir model assumes the monolayer adsorption which the adsorption energy remains unchanged during adsorption process. Meanwhile, Freundlich model demonstrates multilayer adsorption corresponded to the maximum adsorption. The heterogeneity factor of Freundlich isotherm (n) denotes the adsorption type where $n < 1$ assigned to the chemisorption whereas $n > 1$ is assigned to physisorption which Van der Waals and electrostatic force play the role. Apart from aside, the Sips isotherm is a mixture of Langmuir and Freundlich has the strong relation with equilibrium pressure and adsorption temperature. The other modified isotherm derived from Langmuir is Toth isotherm with higher accuracy as the three parameters model compared to the rest of the abovementioned isotherm model. This isotherm model accounts for multi-layered sorption heterogeneity at low and higher levels of adsorbate concentration (Gautam *et al.* 2023).

From the result, it is also implied that the Pb^{2+} adsorption took place on the active sites of $-\text{NO}_2$ in the adsorbent as the monolayer configuration, which is simply illustrated in Figure 12. This interaction supported the Langmuir isotherm model which has the linearity factor (R^2) is close to 1 according to the calculation provided in Table 4. It can be proven the suitable model of this adsorption Pb^{2+} using sty- $\text{NO}_2/\text{Fe}_3\text{O}_4$ is Langmuir compared to Freundlich, Sips, and Toth. In the particularly side, due to exist as hybrid model of Langmuir and Freundlich, Sips isotherm model is more appropriate for heterogenous structure. This assumption also is unlikely proper with the adsorbent material of sty- $\text{NO}_2/\text{Fe}_3\text{O}_4$ which the functional group only consist of NO_2^- which would be interact with Pb^{2+} ion. Meanwhile, the Toth isotherm is also mainly used for gaseous system, thus it is less suitable for applying in solid-liquid adsorption systems (Mozaffari Majd *et al.* 2022), which could not demonstrate with the curve for this study.

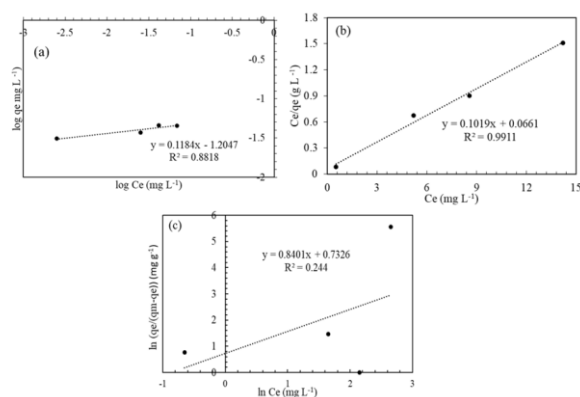


Figure 11. Isotherm adsorption model of (a) Freundlich, (b) Langmuir, and (c) Sips

From the curve, isotherm data could be calculated and was presented in Table 4. The data informs that the linearity correlation factor (R^2) for Langmuir Model is higher, and close to 1, than that of Freundlich Model. Accordingly, it is proven that the adsorption is well-fitted with Langmuir model.



Figure 12. The interaction of Pb^{2+} with NO_2 anionic group from the adsorbent

Table 5. Kinetic parameters of sty- NO_2/Fe_3O_4 adsorbent 33.3 wt%

Pseudo-first-order		Pseudo-second-order	
q_i ($mg\ g^{-1}$)	3.129	q_e ($mg\ g^{-1}$)	7.375
k (min^{-1})	-0.0011	k ($g\ mg^{-1}\ min^{-1}$)	0.131
R^2	0.7796	R^2	0.9994

Table 6. Isotherm adsorption model parameters

Isotherm Freundlich		Isotherm Langmuir		Isotherm Sips	
K_f ($mg\ g^{-1}$)	0.062	K_L ($L\ mg^{-1}$)	1.542	K_s	0.059
n	8.446	q_m ($mg\ g^{-1}$)	9.814	n	1.19
R^2	0.8818	R^2	0.9911	R^2	0.244

4.3.7. The presence of Pb^{2+} adsorbed on the sty- NO_2/Fe_3O_4 adsorbent

The adsorbed Pb^{2+} on the adsorbent was also detected based on its SEM and EDX images, that were presented in Figure 13 and Figure 14, respectively. The SEM image of sty- NO_2/Fe_3O_4 after adsorption exhibits the presence of additional ordered spaced particles, that should be the adsorbed Pb.

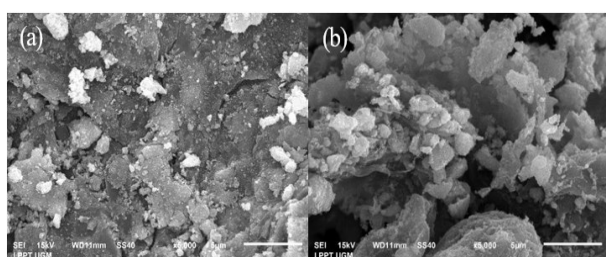


Figure 13. SEM images of sty- NO_2/Fe_3O_4 (a) before adsorption and (b) after Pb^{2+} adsorption

The adsorbed Pb^{2+} was further detected quantitatively based on their EDX spectra. The data from the EDX spectra, was summarized into Table 5.

It can be seen in the Table 5 that in the styrofoam adsorbent after adsorption, the presence of Pb was detected as much as 0.9 wt%, which was not found in the adsorbent before used for absorption. It is clearly evidence that the Pb^{2+} has been successfully adsorbed.

Table 7. The composition of the sty- NO_2/Fe_3O_4 before and after Pb^{2+} adsorption

Element in the sty- NO_2/Fe_3O_4	Content (% w)	
	Before adsorption	After adsorption
C	47.07	49.93
N	14.84	14.29
O	23.61	20.69
Fe	14.48	13.34
Pb	-	0.75

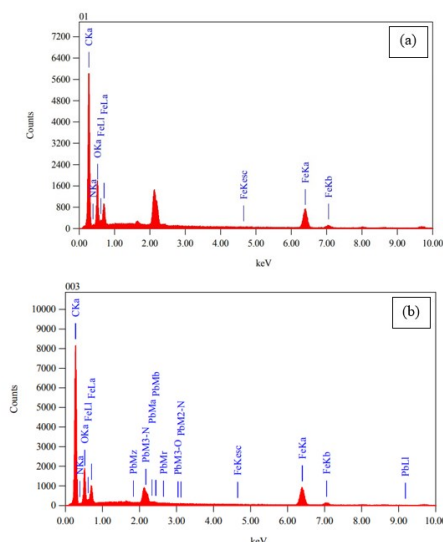


Figure 14. EDX spectra (a) sty- NO_2/Fe_3O_4 before adsorption and (b) sty- NO_2/Fe_3O_4 after adsorption

5. Conclusion

It can be recapitulated, that nitrated-magnetic-styrofoam of sty- NO_2/Fe_3O_4 adsorbent was successfully produced and 33.3 wt% of Fe_3O_4 fraction in the adsorbent showed

good adsorption capacity and separability effectiveness. The optimum condition of the adsorption of $10 \text{ mg L}^{-1} \text{ Pb}^{2+}$ in a 50 mL solution was reached by 30 mg of the adsorbent weight within 60 minutes and at pH 6 with an effectiveness of about 90%. This study plotted in three isotherm adsorption that are Langmuir, Freundlich, and Sips in which the Langmuir model give best-fitted among others with an adsorption capacity of 9.81 mg g^{-1} . The adsorption kinetics well matches to a pseudo-second-order with an adsorption rate constant of $0.131 \text{ g mg}^{-1} \text{ min}^{-1}$. Based on the isotherm and kinetic model, the adsorption of Pb^{2+} by sty- $\text{NO}_2/\text{Fe}_3\text{O}_4$ adsorbent is parallel with the chemisorption mechanism.

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