REMOVAL OF Pb(II) FROM AQUEOUS SOLUTION BY PINEAPPLE PLANT STEM

(Penyingkiran Pb(II) dari Larutan Akueus Menggunakan Batang Tumbuhan Nanas)

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Abstract

The excessive release of lead (Pb) ions into water stream and large production of agricultural wastes cause water and land pollution. Adsorption is useful in eliminating Pb(II) from water environment. The potential use of agricultural waste, pineapple plant stem as adsorbent to reduce the amount of Pb(II) in aqueous solutions was investigated. The material was modified with oxalic acid (OA) to improve the adsorption efficiency of Pb(II). Adsorption isotherms and kinetics were determined for the adsorption of Pb(II) on natural pineapple plant stem (NPPS) and OA modified pineapple plant stem (OAPPS) from aqueous solution in batch studies. The adsorption capacity of Pb(II) on pineapple plant stem depends considerably on the solution pH, in which the amount of Pb(II) adsorbed increased with increasing solution pH, reached its maximal with 14.25 mg/g at pH 5 and 30.47 mg/g at pH 4 for NPPS and OAPPS, respectively. The adsorption performance of the adsorbents was also studied at different initial Pb(II) concentrations (50 – 150 mg/L), it was observed to be less affected at higher initial Pb(II) concentration. The adsorption isotherm was then investigated and the equilibrium data were well fitted with the Langmuir isotherm model with 13.30 and 27.70 mg/g as the calculated maximum capacities for NPPS and OAPPS, respectively. The adsorption of Pb(II) onto NPPS and OAPPS reached equilibrium after 60 minutes at all concentrations studied. The kinetics data were found to follow the pseudo-second order model.

Keywords: adsorption, lead, oxalic acid, pineapple plant stem

Abstrak

Pelepasan ion-ion plumbum (Pb) yang berlebihan ke dalam aliran air dan pengeluaran sisa pertanian yang banyak menyebabkan pencemaran air dan tanah. Penjerapan amat berguna untuk menyingkirkan Pb(II) dari air. Penyelidikan atas penggunaan sisa pertanian, iaitu batang nanas sebagai penjerap untuk mengurangkan Pb(II) dalam larutan akues telah dilakukan. Tambahan pula, batang nanas telah dimodifikasi dengan asid oksalik untuk meningkatkan kecekapan penjerapan Pb(II). Penjerapan isotherma dan kinetik Pb(II) atas tumbuhan nanas semulajadi (NPPS) dan yang dimodifikasi (OAPPS) daripada larutan akues dijelaskan melalui kajian kumpulan. Kapasiti penjerapan Pb(II) pada batang tumbuhan nanas sangat bergantung kepada pH, di mana kapasiti penjerapan meningkat dengan peningkatan larutan pH dari 1 hingga 4, mencapai maksimal dengan 14.25 mg/g pada pH 5 untuk NPPS dan 30.47 mg/g pada pH 4 untuk OAPPS. Prestasi jerapan batang nanas juga diuji dengan pelbagai kepekatan ion logam (50 – 150 mg/L), dan diperhatikan memberi kesan yang rendah dengan kepekatan yang lebih tinggi. Data keseimbangan penjerapan didapat bersesuaian dengan model isoterma Langmuir dengan 13.30 mg/g untuk NPPS dan 27.70 mg/g untuk OAPPS sebagai kapasiti maksima yang dikira oleh model. Penjerapan Pb(II) ke NPPS dan OAPPS mencapai keseimbangan selepas 60 minit pada semua kepekatan yang dikaji. Data kinetik didapat mengikuti model kinetik tertib pseudo-kedua.

Kata kunci: penjerapan, plumbum, asid oksalik, batang tumbuhan nanas
Introduction

Water is the most important resource for human being; however, water pollution becomes a serious worldwide environmental concern. Heavy metals, especially lead (Pb) is widely used for industrial purposes such as battery manufacturing, painting, metal plating and mining. The release of untreated industrial effluent to water environment affects large area of the water sources contaminated with heavy metals. Lead (Pb) is highly toxic and poses danger to living things [1, 2]. The Pb ions accumulate in living tissues damage the vital organs and systems, and eventually disrupt the normal metabolic functioning of body [3]. World Health Organization [4] has set the maximum Pb(II) concentration in drinking water at 0.01 mg/L. Therefore, it is essential to remove Pb(II) from water to minimize the lead poisoning through water drinking.

The common chemical treatment procedures for removal of heavy metal ions from aqueous solution such as ion exchange [5], flotation [6], membrane filtration [7] and electrochemical treatment [8] are efficient in reducing metal ions in water but are expensive to operate. Hence, these methods do not likely satisfy the requirement of industrial wastewater treatment industries which hope for inexpensive, cleaner and greener technology. Recently, researchers start to adopt adsorption with low cost materials as adsorbents to eliminate metal ions from aqueous solution. The adsorption with agricultural waste materials is considered suitable for the industries uses as it promotes the reuse of unwanted wastes, cost effective [9], possible to regenerate adsorbents and recover metals, as well as minimize the sludge generation.

The agricultural wastes consist of cellulose, hemicellulose and lignin which have various functional groups that can bind the metal cations from solution [10]. The properties are useful in the heavy metal ions adsorbing. Several adsorbents such as rice straw [11], coconut shell [12], ginkgo leaf, peanut shell [13], coffee husk [14], orange peel, lemon peel, banana peel and watermelon peel [15] have been used and tested for Pb(II) removal from aqueous solution. Pineapple is a common tropical fruit, used in food industry and consumed globally. After harvested from the farm, the stem was discarded as waste in municipal landfills or open burning. The plant stem represents about 60% of the total weight of the pineapple plant. The huge generation of pineapple waste and poor waste management lead to serious air and land pollutions. The disposal problem could be handled by reutilizing the pineapple plant stem (PPS) as an adsorbent in adsorption. This gives advantages to the society as value-added products will be produced from unused materials.

The usage of natural agricultural waste products poses drawbacks. Lignocellulosic plant materials may release organic matters to aquatic environment thus leaving secondary pollutants to the aqueous solution. The leaching of organic matter can be lowered by washing the adsorbents before using or modifying adsorbents in an appropriate manner. The pre-treatment and chemical modifications increase the surface area of adsorbent and add more surface functional groups on the adsorbent. Thus, the adsorbent capacity to adsorb metal ions might be improved. Oxalic acid (OA) is a simple acid and considered to be less toxic, frequently used in pharmaceutical industry. The carboxylic sites on OA are expected to add functional groups on the surface of adsorbent, thus give higher adsorption capacity of the modified adsorbent.

This study aims to assess the adsorption potential of the adsorbents prepared from the natural and OA modified pineapple plant stem for the removal of Pb(II) ions from aqueous solutions. The interactive effects of process parameters such as the pH of solution, initial Pb(II) concentrations and the contact time on the adsorption capacity of the adsorbent were studied. Furthermore, adsorption isotherms as well as kinetics models were discussed.

Materials and Methods

Preparation of adsorbents

The procedures to prepare the natural pineapple plant stem (NPPS) adsorbents were adopted from Chan et al. [16]. The stems were first cut into pieces, then ground and sieved to particle size range 105 to 250 µm. Then, the particles were boiled with distilled water thrice before they were dried at 50 °C for 24 hours. The prepared NPPS were kept in air tight containers and ready to be used and undergo chemical modification.
The oxalic acid (OA) treatment of PPS was performed and modified according to previous method reported by Marshall et al. [17]. The dried PPS was added to 0.5 M OA at ratio of 1:20, agitated for 30 minutes at room temperature. The liquid mixture was then discarded and the residue was spread in tray. The wet PPS residue was activated at 120 °C in an oven for 90 minutes. The OA modified PPS (OAPPS) was then washed repeatedly with distilled water until neutral pH of filtrate was obtained. Finally, OAPPS was dried overnight in oven at 50 °C then it was kept in air tight container for further use.

**Preparation of heavy metal stock solution**

The heavy metal Pb(II) solution was prepared. A quantity of 1.5905 g Pb(NO$_3$)$_2$ crystal was dissolved in 1000 mL of distilled water to prepare the desired concentration of 1000 mg/L. The stock solution prepared was diluted to various concentrations ranged 50 to 150 mg/L for batch adsorption studies.

**Batch adsorption studies**

The batch experiment was carried out at room temperature to determine the adsorption capacity towards Pb(II) by mixing 25 mL of Pb(II) solution in centrifuge tube. An orbital shaker was set at 150 rpm, mixture was shaken at the agitation rate. A Pb(II) solution without adsorbents was served as control and to determine the initial concentration of the Pb(II) solutions prepared. The pH of the solutions was maintained and determined using pH meter. The analyte was collected and the final Pb(II) concentrations were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES) instrument (Perkin Elmer, model Optima 2000DV). The steps mentioned were repeated under different conditions: solution pH, initial Pb(II) concentration and contact time. The experiments were conducted in triplicates. The initial and final concentration of Pb(II) were recorded and adsorption capacity was calculated using equation 1:

\[
\text{Adsorption capacity (mg g$^{-1}$)} = \frac{(\text{Initial concentration - Final concentration}) \times \text{volume of solution}}{\text{Weight of adsorbent}}
\]

The effect of solution pH on the Pb(II) adsorption capacity by NPPS and OAPPS was studied. The prepared adsorbents with 0.05 g was added into a series of 100 mg/L Pb(II) solution and were shaken for 5 hours. The initial pHs of solution were varied from 1 to 7 by adjusting with 0.01 M HNO$_3$ and 0.1 M NaOH solution. After 5 hours, the residual solutions were analyzed using ICP-OES.

The effect of initial Pb(II) concentrations and contact time was investigated. The NPPS and OAPPS with dose of 0.05 g/25 mL were added into series of 50, 75, 100, 125 and 150 mg/L and were shaken at different time intervals: 5, 10, 15, 30, 60, 90, 120 and 180 minutes. The supernatants were collected at the mentioned time. The residual solutions were analyzed using ICP-OES. Later, the experimental data were fitted to Langmuir and Freundlich isotherm models, as well as pseudo-first and pseudo-second kinetics models to study the adsorption mechanism.

**Results and Discussion**

The study of the factors affecting the efficiency of heavy metal ions adsorption is important for the interest of industry. The performance of the Pb(II) adsorption is affected by solution pH, initial metal ion concentration and contact time. Studies on these factors were carried out to investigate the relationship between the adsorbate and adsorbents and propose the mechanism in the adsorption of Pb(II) by NPPS and OAPPS.

**The effect of solution pH**

The solution pH may influence the surface charge of adsorbent and the chemistry of metal [18]. The effect of solution pH on the Pb(II) removal was investigated with pH variation from 1 to 7 and are presented in Figure 1. The Pb(II) adsorption from aqueous solution may dependent on the pH value.
The results portrayed that the Pb(II) adsorption increased with increasing pH till a maximum, then decreased afterwards. The maximum adsorption capacities were achieved at pH 5 with 14.25 mg/g and pH 4 with 30.47 mg/g of Pb(II) adsorption on NPPS and OAPPS, respectively at 25 °C.

The solution pH affects the surface characteristic of the adsorbents. This is due to the pH point of zero charge (pH_{pzc}) difference in each adsorbent. NPPS and OAPPS have neutral charges at pH 4 and pH 2.4, respectively. Adsorbents are negatively charged at solution pH higher than its pH_{pzc}. Hence, a lower pH_{pzc} means that the surface charge of adsorbent becomes negative at a lower pH, therefore the cationic Pb(II) ions at a wider range can be attracted.

In highly acidic solution (< pH 4), the functional groups, especially carboxyl groups on the adsorbents were protonated, gave a positive charge on the adsorbent surface. There might be a great electrostatic repulsion between the positive Pb(II) ions and the positive adsorbent species. Furthermore, the presence of hydrogen and hydronium ions creates a competitive environment for the available binding sites. This phenomenon lowers the adsorption capacity of both NPPS and OAPPS.

The carboxyl groups were less protonated when the solution pH was increased. When the pH values increased (pH 4 - 5), the adsorbent surface becomes less positive and the concentration of the competing positive ions (H^+ and H_3O^+) decreases, thus more electrostatic attraction occurred between Pb(II) and adsorbents surface. As a result, the adsorption capacity observed was found to be improved in slightly acidic solution.

The solution pH affects the metal speciation as well. At higher pH (> pH 5), the adsorption capacity was decreased. This is mainly due to the formation of hydroxyl metal complexes when Pb(II) started to precipitate. The basic environment facilitates the formation of precipitate complex with metallic ions attached to the hydroxide ions forming Pb(OH)_2 and negatively charged Pb(OH)_3^- complex ions [19]. This again creates repulsion between the negative adsorbent species and negatively charged metal ions. In the effort to prevent precipitation, experiments were carried out at pH < 6 to make sure the Pb(II) were soluble and avoid the formation of metal hydroxides.

**Effect of initial concentration and contact time**

The initial Pb(II) concentrations were varied from 50 to 150 mg/L and batch studies were conducted at different time intervals to study the adsorption equilibrium and kinetics, while other factors were kept constant. The Pb(II) uptake was conducted over a period of 180 min at room temperature.

As shown in Figure 2(a), the Pb(II) adsorption by NPPS was less affected by the initial metal ion concentration. The maximum amount of Pb(II) adsorbed at different metal ion concentrations investigated was between 12.89 to 14.57
mg/g. There is less significance in Pb(II) uptake by NPPS at different initial Pb(II) concentrations. On the other hand, the Pb(II) adsorption by OAPPS was likely to be affected by the initial metal ion concentration as shown in Figure 2(b). The modified adsorbent adsorbed 15.29 mg/g Pb(II) at the lowest, 50 mg/L initial Pb(II) concentration. The adsorption performance was then sharply increased to 24.91 mg/g at 75 mg/L Pb(II) concentration and showed less difference in the adsorption capacity (25.98 mg/g - 27.53 mg/g) from 100 mg/L to 150 mg/L Pb(II) concentration.

Figure 2. The effect of initial concentration and contact time onto (a) NPPS and (b) OAPPS

Mass transfer resistance of metal ions between the solution phase and the solid adsorbent phase occurred during adsorption and the initial adsorbate concentration serves as driving force to overcome it [20, 21]. At lower Pb(II) concentration, most Pb(II) ions could bind on the adsorbent surface as there is a large ratio of available adsorption site between the amount of Pb(II) present in the solution. As the initial Pb(II) concentration increased, the ratio of unoccupied binding site is getting smaller. The adsorption site was saturated with Pb(II) ions at constant mass of adsorbent, causing the more Pb(II) ions left unadsorbed in the solution. Maximum adsorption sites were occupied at high initial metal ion concentration; hence, there is less significance in the adsorption performance.

The adsorption capacity of NPPS and OAPPS increased with increasing contact time and reached the maximum and equilibrium after 60 minutes (Figure 2). At the initial phase or the time period from 0 to 30 minutes, a rapid adsorption was observed. This is mainly due to the unoccupied binding sites mostly available to interact with the Pb(II) ions [22]. As the adsorption time extended, the adsorption sites were majorly covered, thus reducing the
opportunity of Pb(II) ions to interact with the functional groups on the adsorbents. Upon reaching equilibrium, the saturated binding sites did not facilitate the Pb(II) adsorption giving an almost constant adsorption capacity. It was clearly observed that the equilibrium time was not dependent on the initial metal ion concentration. The results revealed that same equilibrium time can be achieved for all the initial Pb(II) concentrations investigated (50 – 150 mg/L).

**The adsorption isotherm**

The experimental data were fitted to two adsorption isotherm models: Langmuir and Freundlich models and studied. Langmuir [23] and Freundlich [24] isotherms are used to explain the mechanism of adsorption and the relationship between the amount of adsorbed metal ion and the concentration of metal ion remained in solution.

The Langmuir isotherm model proposes a monolayer adsorption of metal ion on the adsorbent surface. Besides, it also assumes that the number of adsorption sites are fixed, where there will be no adsorption occurred onto the adsorbent surface when the available binding sites are fully occupied. The linear form of the Langmuir isotherm is presented by equation 2:

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}}} C_e + \frac{1}{q_{\text{max}} K_L}
\]

where \( C_e \) refers to the equilibrium concentration of metal ions (mg/L); \( q_e \) is the amount of metal ions adsorbed at equilibrium (mg/g); \( q_{\text{max}} \) is the maximum amount or the amount of metal ions adsorbed; \( K_L \) is the Langmuir constant defining the adsorption capacity or the adsorption energy. A linear graph with \( C_e/q_e \) against \( C_e \) was plotted. The values of \( q_{\text{max}} \) and \( K_L \) can be calculated from the slope and the intercept of the isotherm.

The Freundlich isotherm model on the other contrary suggests multilayer metal ion adsorption. The amount of adsorbed metal ion on the surface of adsorbent is expected to be increased with the increasing adsorbate concentration. This model is linearized as shown in equation 3:

\[
\log q_e = \frac{1}{n} \log C_e + \log K_F
\]

where \( K_F \) refers to the Freundlich constant defining the capacity of the adsorption. The linear graph will yield an intercept of \( \log K_F \) and a slope of \( \frac{1}{n} \).

The parameter values for Langmuir and Freundlich isotherms are listed in Table 1. The \( R^2 \) values obtained from Langmuir models for Pb(II) adsorption by NPPS and OAPPS have correlation coefficient values, which are 0.9992 and 0.9997, respectively, whereas Freundlich models were 0.9228 and 0.9505 for NPPS and OAPPS, respectively. The correlation values obtained from the Langmuir models were relatively higher as compared to Freundlich’s correlation values, suggesting that the Langmuir model is highly applicable to the adsorption system.

| Parameters   | NPPS  | OAPPS  |
|--------------|-------|--------|
| Langmuir q_{max} (mg/g) | 13.30 | 27.70  |
| K_L (L/mg)   | 5.1130 | 8.6288 |
| R^2          | 0.9992 | 0.9997 |
| Freundlich K_F (L/mg) | 8.7418 | 10.4304 |
| n            | 12.4688 | 4.9407 |
| R^2          | 0.9228 | 0.9505 |
This indicates that the monolayer adsorption of Pb(II) occurred on NPPS and OAPPS. The adsorbent, OAPPS have a higher Langmuir isotherm constant, $K_L$ value. This indicates that Pb(II) ions have higher affinity to bind to the functional groups on OAPPS, resulted higher maximum adsorption capacity over OAPPS.

The adsorption kinetics

The contact time of adsorption determines the kinetics, then used to describe the rate of Pb(II) adsorption and the Pb(II) adsorption behavior onto NPPS and OAPPS.

The pseudo-first and pseudo-second order models are linearized as shown in equations 4 and 5, respectively.

$$\ln(q_e - q_t) = -k_1 \cdot t + \ln q_e$$  \hspace{1cm} (4)

$$\frac{t}{q_t} = \frac{1}{q_e} \cdot t + \frac{1}{k_2 q_e^2}$$  \hspace{1cm} (5)

where $q_e$ is the amount of metal ions adsorbed at equilibrium (mg/g); $q_t$ refers to the amount of metal ions adsorbed at time, $t$ (mg/g) respectively; $k_1$ and $k_2$ refer to the rate constant of pseudo-first order and pseudo-second order, respectively.

Based on Table 2, the experimental data was best fitted with pseudo-second order model, suggesting that the adsorption might be a chemical process [25]. Chemical adsorption involved electron sharing or transfer limits the adsorption rate. The Pb(II) ions adsorption onto NPPS and OAPPS involved two phases. Initially, the adsorption is fast and equilibrium phase was attained. Afterwards, the Pb(II) adsorption was slow and proceed with less significance in the capacity with longer time.

### Table 2. Comparison of experimental and theoretical adsorption capacities of pseudo-first order and pseudo-second order of adsorption at 150 mg/L Pb(II) solution

| Parameters          | NPPS  | OAPPS |
|---------------------|-------|-------|
| Experimental values | $q_e, \text{exp}$ (mg/g) | 12.25  | 27.65  |
| Pseudo-first order  | $q_e, \text{cal}$ (mg/g) | 0.63   | 3.68   |
|                    | $k_1$ (1/min)       | 0.0102 | 0.0232 |
|                    | $R^2$               | 0.4411 | 0.7079 |
| Pseudo-second order | $q_e, \text{cal}$ (mg/g) | 12.13  | 27.53  |
|                    | $k_2$ (g/mg·min)   | 84.87  | 0.0197 |
|                    | $R^2$               | 0.9994 | 0.9997 |

Adsorption mechanism and comparative adsorption study

The pineapple plant stem consists of intricate surface structure and composition, thus Pb(II) ions might interact in a number of possible ways on the surface of agro-waste adsorbent during adsorption. Based on this study, two main adsorption mechanisms were proposed, namely electrostatic attraction and monolayer chemisorption took place during the Pb(II) adsorbing by NPPS and OAPPS.

The capacities of Pb(II) ion adsorption onto NPPS and OAPPS were observed to depend on solution pH. The test results presumed that the adsorption mechanism involved the electrostatic interactions during the process. The optimum pH for Pb(II) adsorption by NPPS and OAPPS was 5 and 4, respectively. Thus, the batch adsorption studies were carried out in solution pH 4 - 5. In solution pH > 5, the dominant metal species in aqueous solution were lead hydroxide [Pb(OH)$_2$] and Pb(OH)$_3^-$ complex ions whereas Pb$^{2+}$ and Pb(OH)$^+$ were the foremost metal
ions exist in solution pH < 5. The functional groups on NPPS and OAPPS were deprotonated at solution pH > 4. The adsorbents then act as negative species, attracted the dominant cationic Pb metal ions.

The adsorption isotherm and kinetics studies suggested that the Pb(II) adsorption onto NPPS and OAPPS to be a physicochemical reaction, involved both physical adsorption and monolayer chemisorption. The fast adsorption was observed at the initial phase of Pb(II) adsorption by NPPS and OAPPS, proposed the occurrence of physisorption and may be due to the macrospores of both adsorbents. Later, the adsorption process slowed down, chemical reaction, namely ion-exchange was anticipated. The abundant hydroxyl functional groups on NPPS might interact with the Pb(II) ions in the mechanisms shown in Equations 6 and 7.

\[
C_n\text{-OH} + \text{Pb}^{2+} \rightarrow C_n\text{-OPb}^+ + \text{H}_2\text{O}^+ \quad (6)
\]

\[
(C_n\text{-OH})_2^+ \text{Pb}^{2+} \rightarrow (C_n\text{O})_2\text{Pb} + 2\text{H}^+ \quad (7)
\]

After chemical modification with OA, more carboxyl functional groups present on the surface of OAPPS. Thus, ion exchange mainly occurred between the Pb(II) ions and electrons from carboxyl groups on the adsorbent and controlled the adsorption process. The possible mechanisms were shown below (equations 8 and 9):

\[
C_n\text{-COOH} + \text{Pb}^{2+} \rightarrow C_n\text{-COO}\text{Pb}^+ + \text{H}_2\text{O}^+ \quad (8)
\]

\[
(C_n\text{-COOH})_2^+ + \text{Pb}^{2+} \rightarrow (C_n\text{-COO})_2\text{Pb} + 2\text{H}^+ \quad (9)
\]

The capacities of the Pb(II) adsorbing by NPPS and OAPPS with the adsorbents reported in the text were compared and listed in Table 3.

| Agricultural wastes            | Maximum capacities (mg/g) | References |
|--------------------------------|---------------------------|------------|
| Activated carbon               | 8.70                      | [13]       |
| Peanut shell                    | 11.26                     |            |
| NPPS                           | 12.13                     | This study |
| Citric acid modified rice straw | 18.98                     | [11]       |
| Orange peel                    | 19.15                     | [15]       |
| Banana peel                    | 19.18                     |            |
| Coffee husk                    | 19.23                     | [14]       |
| Lemon peel                     | 19.32                     | [15]       |
| Watermelon peel                | 19.39                     |            |
| Ginkgo leaf                    | 24.04                     | [13]       |
| Coconut shell                  | 26.14                     | [12]       |
| OAPPS                          | 27.53                     | This study |

Table 3 shows that both NPPS and OAPPS are capable to uptake Pb(II) ions from aqueous solution. The adsorbent NPPS has a moderate adsorption capacity of 12.13 mg/g as it contains beneficial functional groups for adsorption. It was hypothesized that the carboxyl groups play a vital role in Pb(II) adsorption from aqueous solution by replacing the \(H^+\) protons from the carboxyl groups with the \(\text{Pb}^{2+}\) ions and formed carboxylate groups. The adsorption capacity of Pb(II) on OAPPS was doubled to 27.53 mg/g after the chemical modification of PPS with OA. When heated, the
oxalic acid converted to oxalic acid anhydride and further reacted with the hydroxyl groups on PPS. Thus, carboxyl groups were added to the surface of PPS, led to increase in the adsorption of Pb(II) ions. Generally, NPPS and OAPPS showed great potentials to be used as adsorbents in wastewater treatment and industries for heavy metal ion removal from aqueous solution.

**Conclusion**

In this work, the agricultural waste, pineapple plant stem was successfully utilized as adsorbents for Pb(II) removal from aqueous solution. Furthermore, pineapple plant stem was undergone pre-treatment and chemical modification with oxalic acid. Overall, the oxalic acid modified pineapple plant stem (OAPPS) showed improved performance than the natural pineapple plant stem (NPPS) involved in the study. Batch studies were carried out under different conditions: solution pH, initial Pb(II) concentration and contact time to evaluate the adsorption efficiency of Pb(II) ions on NPPS and OAPPS. The Pb(II) adsorption was enhanced with increasing solution pH values and gave optimum pH at 5 with 14.25 mg/g and 4 with 30.47 mg/g Pb(II) adsorbed by NPPS and OAPPS, respectively. The Pb(II) adsorption capacity by both adsorbents improved with increasing initial Pb(II) concentration. Besides, it was observed that the adsorbents performances were less affected at higher initial metal ion concentration. The adsorption equilibrium data was well fitted with the Langmuir isotherm, proposing monolayer adsorption. Meanwhile, the Pb(II) ions adsorption onto NPPS and OAPPS reached equilibrium at 60 min and followed pseudo-second kinetics order model. The model suggests that the Pb(II) adsorption mechanism involved chemisorption. The results of this work suggest that pineapple plant stem can be an alternative adsorbent for the adsorption process in removing Pb(II) ions from wastewater.

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