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Removal of Lead (Pb) from Aqueous Solutions using Exoskeleton of Black Soldier Fly (BSF)

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Abstract

Lead (Pb) pollution in water sources poses environmental and public health risk. It is important to mitigate the effects by developed an effective remediation method. The potential use of deceased black soldier fly (*Hermetia illucens*) to remove Pb from aqueous solutions was studied. The flies were ground into a fine powder, analyzed, and then subjected to adsorption studies using Pb synthetic aqueous solutions. Results showed that the deceased black soldier flies are effective in removing Pb from aqueous solutions. The findings lead to the development of resource-efficient heavy metal remediation methods that use the large biomass of black soldier flies.

Keywords: Black soldier fly; adsorption; plumbum; isotherm

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1.0 Introduction

Heavy metal poisoning in the environment has resulted from rapid industrialization and urbanization, and their rates of mobilization in the environment have dramatically increased since the 1940s (Ali et al., 2019). Numerous sectors, including electroplating, printing, dyeing, oil painting, electrolysis, insecticides, and medicine, employ heavy metals extensively. Because of these numerous sectors, different organic and inorganic contaminants are present in the industrial discharge (Zhou et al., 2021). Plumbum, commonly known as lead (Pb), is discharged into the soil, air, and aquatic habitats as a result of various industrial processes, such as those used in the production of paint, explosives, pigments, photographic materials, printing, storage batteries, and television tubes. Nearly every organ and system in the human body is susceptible to lead. The US Environmental Protection Agency (USEPA) and the International Agency for Research on Cancer (IARC) have designated it as a potential human carcinogen due to its toxicity (Chowdhury et al., 2022).

Many techniques, and methods in removing heavy metals being use and implement in the industries (Qasem, Mohammed & Lawal, 2021). A specific technique for removing heavy metal ions has been the subject of recent studies, however, Renu et al. (2017) mentioned that the other methods have inherent flaws such producing a lot of sludge, being ineffective, needing delicate operating conditions, and being expensive to dispose of, hence adsorption is the most effective. Therefore, adsorption is one of the investigated techniques for the purification of wastewaters and is a promising, economical, eco-friendly, and effective process. The second-most prevalent natural biopolymer, chitin (poly-(1,4)-N-acetyl-D-glucosamine), has gained scientific interest as a low-cost adsorbent for hazardous metals (Anastopoulos et al., 2017). It has a molecular

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weight of 203.2 g/mol and can be found in the exoskeleton of arthropods like crustaceans (crabs, lobsters, and shrimp) and the cell walls of fungus (Begum et.al., 2018).

Bhavsar et.al., (2021), said that in the past few years, there has been a noticeable rise in interest in insects as valuable sources of lipids, proteins, and chitin as well as waste biomass bio converters. Black soldier fly (BSF) is a species native to South America but currently cosmopolitan, containing rich source of chitin (20% form BSF exuviae). Even though there is much research has been conducted trying low-cost adsorbent, new adsorbent still needed to be studied due to the increasing demand for industrial wastewater treatment. This study was carried out to identify the potential of BSF in removing Pb from aqueous solutions by observing the adsorption efficiency in different operating condition and analyzing the interaction of BSF and Pb using adsorption isotherm and kinetic model.

2.0 Literature Review

The annual production of industrial wastewater has been negatively impacted by the rapid industrialization of the world. Tens of millions of cubic meters per day of the total wastewater discharged globally came from industrial waste. According to records, between 80 and 90 percent of the wastewater in underdeveloped nations is immediately released, untreated, into surface water bodies (Popoola & Grema, 2020). As science and technology advance, more heavy metals are being used, particularly in industries, which is leading to numerous environmental issues (Putri & Syafiq, 2019). Due to the presence of copper, chromium, zinc, nickel, and cadmium, the discharge of heavy metals from industrial processes is more dangerous (Al Moharbi et.al., 2020).

2.1 Toxicological of lead

Lead is persistent in the environment and can be deposited from sources of lead air pollution into soils and sediments. Reduced development and reproduction in plants and animals, as well as neurological consequences in vertebrates, can be caused by elevated lead levels in the environment (United States Environmental Protection Agency, 2016). Pb from the environment can compete with other metals present in and on plant surfaces, perhaps impeding photosynthesis and, in sufficiently high quantities, harming plant development and survival. It also can go up to the food chain through contaminated soils and plants which cause harm to the neurological, renal, reproductive, hematopoietic and cardiovascular systems of animals (Boldyrev, 2018). A child's exposure to lead can have major negative health impacts, including damage to the brain and neurological system, slower growth and development, cognitive and behavior issues, and hearing and speech issues. This may result in a lower IQ, a reduced capacity for paying attention, and poor academic performance (Centers for Disease Control and Prevention, 2020). Additionally, it can worsen the baby's growth before birth and raise the risk of miscarriage (Department of Health New York State, 2022).

2.2 Characteristic of adsorbent

Hermetia illucens, sometimes known as the black soldier fly (BSF), is a true fly (Diptera) in the Stratiomyidae family. Although originally from the Americas, it now grows in tropical and temperate locations all over the world. BSF larvae have been utilized in small-scale waste management projects employing substrates such manure, rice straw, food waste, distillers' grains, fecal sludge, animal offal, kitchen garbage, and so on (Wang & Shelomi, 2017). The BSF is one of the insects that has chitin (Zlotko et.al., 2021). Chitin is a desirable biomaterial due to its strong reactivity, chemical stability, and nontoxicity. Their practical accessibility, biocompatibility, and environmentally advantageous qualities are shared by both lignin and chitin. Additionally, both biopolymers were said to exhibit a sorption propensity for heavy metal ions (Duan et.al., 2018).

2.3 Adsorption study on lead

According to a study by Forutan et.al., (2016) on the adsorption of lead by pink shrimp chitin, the equilibrium of adsorption was attained in 0–200 minutes. It was found that the ideal pH, contact time, biosorption dosage, and initial lead concentration were 9, 0-200 minutes, 5 gr/L, and 7.99 ppm, respectively. A 99.7% biosorption efficiency was found to be the best. The equilibrium of biosorption by pink shrimp-produced chitin was characterized by the Freundlich equation and Langmuir model, and the kinetics of the process in the case of both biomaterials was described with a pseudo-second order equation.

The adsorption capabilities of 30% bromine-pre-treated chitosan for lead (II) abatement from water were investigated in the work by Dongre et.al., (2011). By adjusting the pH, bromine loading, sorbent dosage, initial lead concentration, contact time, and temperature, lead adsorptions were examined in batch mode. The maximum sorption capacity of 30% bromine-pre-treated chitosan sorbent was 1.755 g/kg with 85–90% lead removal efficiency, according to the adsorption equilibrium data that was well suited to the Freundlich isotherm.

3.0 Methodology

3.1 Adsorbent preparation

The deceased BSF that were collected from BSF Research Laboratory, Faculty of Health Sciences were washed in running tap water to remove the impurities (Lin et.al., 2021). Then, the flies were dried in an oven at 105°C for 48 hours and grinded with a grinding machine to break the exoskeleton. The fine powder of the flies was further analyzed under the Fourier-transform infrared spectroscopy (FTIR) to assess their elemental composition and surface properties (Soetemans et.al., 2020).

3.2 Adsorbate preparation

A stock solution of 1000 mg/L of Pb was prepared by dissolving a certain amount of chemically pure Pb in distilled water. An aliquot of stock solution then further diluted with distilled water to prepare the desire experimental concentration range between 2 to 10 mg/L. The stock solution

of 0.1 M of hydrochloric acid (HCL) and natrium dioxide (NaOH) were used for the adjustment of pH and was monitored by using a calibrated pH meter (HANNA instruments type).

3.3 Batch adsorption study

Batch adsorption studies were conducted with different concentrations of Pb in a 50 mL of volumetric flasks. The Pb concentrations were examined separately by changing the contact time (30 – 150 mins), initial pH (3-11), Pb concentrations (2 – 10 mg/L), and adsorbents dose (0.2 -1.0 g). Batch adsorption experiments of Pb were conducted in order to determine the equilibrium time and effect of the contact time on the mechanism of heavy metals adsorption onto BSF. The solutions were filtered using Whatman filter paper to separate solid from liquid and analyzed using atomic adsorption spectroscopy (AAS). The amount of Pb absorbed was calculated from the following equation:

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

Where C_o is the initial concentration of heavy metals (mg L^{-1}) while C_e is the equilibrium concentrations of heavy metals (mg L^{-1}), m is the amount of BSF (g), and V is the volume of heavy metal solutions (L). The following formula was used to compute the efficiency percentage (R) of heavy metal removal:

$$R = C_o - \frac{C_e}{C_o} \times 100$$

3.4 Isotherm Studies

The adsorption isotherm was crucial in explaining how the solute interacts with the absorbent, and two models were used which are Langmuir and Freundlich isotherms (Boulaiche et.al., 2019).

Langmuir isotherm

The Langmuir isotherm model presupposes monolayer adsorption on a flat surface. The linear form was given by when a site was filled, no further adsorption takes place is:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}KL} + \frac{C_e}{q_{max}}$$

The slope and intercept of the linear plot of $\frac{C_e}{q_e}$ versus C_e are used to compute the constant (KL), which is related to the adsorption energy, and the maximum adsorption capacity ($q_{max} \text{ mg/g}$).

Freundlich isotherm

For the Freundlich isotherms, this model represents situations in which molecules are adsorbed on heterogeneous surfaces and interact with one another. The linear form is provided by:

$$\log q_e = \log Kf + \frac{1}{n} \log C_e$$

The plot of $\log q_e$ vs $\log C_e$ is used to calculate the constant (Kf), which is caused by the bond energy and the heterogeneity factor ($\frac{1}{n}$), which measures the deviation from the linear component.

Kinetic studies

To identify the step that controls the adsorption of Pb onto the BSF, a kinetic investigation was carried out. Two models which are the pseudo-first-order and pseudo-second-order models, whose linear forms are provided below were examined for these purposes (Boulaiche et.al., 2019):

The following relation presents the pseudo-first-order:

$$\ln (q_e - qt) = \ln q_e - tk_1$$

Where q_e and qt (mg g^{-1}) is the number of heavy metals adsorbed at equilibrium and time t (min), respectively, and k_1 is the rate constant (min^{-1}). The slope and intercept of the linear plot of $\ln (q_e - qt)$ versus t will be used to determine q_e and k_1 , respectively.

The pseudo-second-order equation can be expressed in the following way in the linear form:

$$\frac{t}{qt} = \frac{1}{q_e^2 k_2} + \frac{1}{q_e} t$$

The equilibrium rate constant is k_2 (g/mg min). The plot of $\frac{t}{qt}$ versus t is used to determine the values of q_e and k_2 .

4.0 Findings and Discussion

4.1 Characterization of black soldier fly (BSF)

Fourier Transform Infrared (FTIR) was used to determine the functional group present in the BSF. This has been mentioned by Soetemans et.al., (2020) that since every organic compound has a well-defined resonance frequency in the infrared spectrum, FTIR can be used to examine molecular structure by generating a spectrum indicating the infrared wavelengths that the sample absorbed. As for BSF, Smets et.al., (2020) the dominant adsorption bands are 3449 cm^{-1} , 3109 cm^{-1} , 2932 cm^{-1} , 2891 cm^{-1} , 1662 cm^{-1} and 1624 cm^{-1} , 1560 cm^{-1} , 1415 cm^{-1} , 1379 cm^{-1} , 1315 cm^{-1} , 1157 cm^{-1} , 1116 cm^{-1} , 1074 cm^{-1} and 1027 cm^{-1} , 953 cm^{-1} , 897 cm^{-1} , 702 cm^{-1} , and 561 cm^{-1} . Thus, for this study the result was presented in Fig. 1 which shows the various band of functional groups in the BSF that responsible of the Pb adsorption and the characteristic bands and their meanings are given in Table 1.

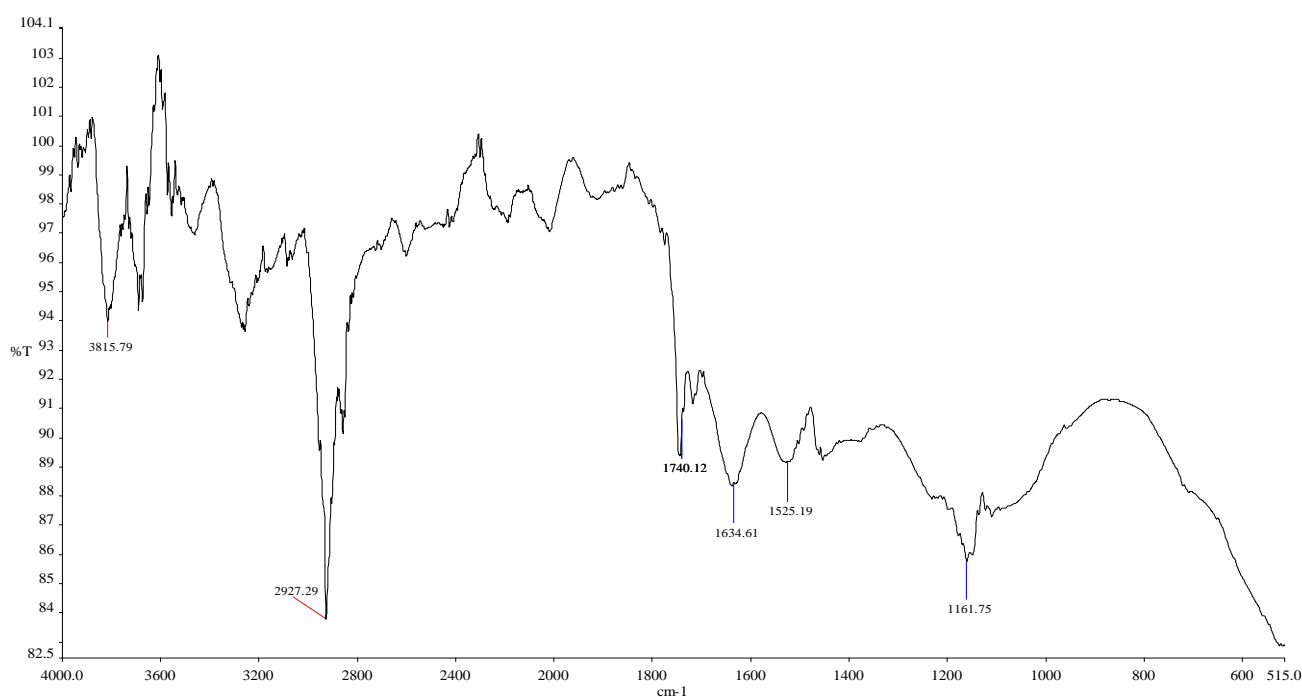


Fig. 1: The FTIR spectra of black soldier fly

Table 1: Summary of FTIR spectra of BSF

Wavenumber (cm^{-1})	Functional Group
4000 – 3584	O-H stretching
3000 – 2500	Vibrations of elongations of C-H bonds in group CH_2 and CH_3
1740	C=O stretching
1634	Valence vibration C=O (Amide I)
1525	Vibration of N-H (Amide II)
1161	Valence vibration of C-N stretching

4.2 Batch adsorption studies

Effect of pH

The pH is the key element in the removal of heavy metals using a variety of techniques, including chemical precipitation, adsorption, and biological approach (Karimi, 2017). Boulaiche et.al., (2019) also mentioned that because the pH already impacts the adsorbate's surface charge and the type of ionic species present in it, it has a significant impact on the heavy metal adsorption. In this study, the effect of pH was examined in the pH region between 3 to 11. The other parameter including adsorbent dosage (0.2 g), initial Pb concentration (2.0 mg/L) and contact time (150 minutes) were kept constant. The relationship between the initial pH of the Pb solution with the adsorption capacity of Pb and the percentage of Pb removal are shown in Fig. 2 below:

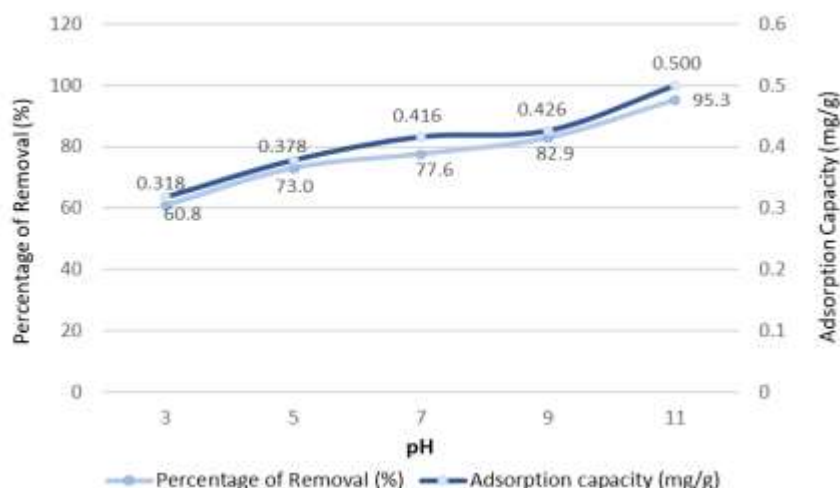


Fig. 2: The percentage of Pb removal and adsorption capacity by the exoskeleton of BSF in various pH region

Figure above shows that the percentage of Pb removal and the capacity of the exoskeleton of BSF to remove Pb increase with the raising pH. The adsorption capacity is increased from 0.318 mg/g to 0.500 mg/g with the increasing initial pH from 3 to 11. The Pb uptake is comparatively lower in acidic pH condition approximately 60.8% but it increased for higher pH value indicating that the percentage of Pb removal reached 95.3%. This indicate that at pH 3, the adsorption capacity is minimal and increases slightly with augmenting the pH to 5, 7, 9 and 11. Due to the increased number of hydrogen ions, which have the ability to compete with metal ions and reduce adsorption efficacy, Pb removal was only moderately effective under low pH circumstances (Begum et.al, 2018). Therefore, the high concentrations and high mobility of H^+ ions, which are adsorbed more than heavy metal ions, are responsible for the drop, in adsorption rate at low pHs (Boulaiche et.al., 2019).

Ting et.al., (2019) stated that when the pH of the solution was raised, the protonation of the carboxyl groups decreased. More electrostatic attraction developed between the Pb ion and the adsorbent surface as pH values rose because the adsorbent surface became less positive and the concentration of the competing positive ions (H^+ and H_3O^+) decreased. As a result, the protonation reaction of Pb obtained more negative charges which enhance the electrostatic interaction between Pb and chitin in the BSF. Therefore, the optimum pH condition selected for adsorption of Pb in aqueous solution using the exoskeleton of BSF is at pH 11.

Effect of adsorbent dosage

At this stage, the experiments were done under the conditions described at the previous stage with constant pH of 11, contact time 150 minutes, initial Pb concentration at 2.0 mg/L and variable adsorbent dosage. In general, the amount of a solute that is adsorbed increases as the concentration of an adsorbent rises because more active exchangeable adsorption sites result from higher adsorbent concentrations. However, interference brought on by the interaction of an adsorbent's active sites might cause the overall solute adsorption per unit weight of an adsorbent to decrease after an increase in adsorbent concentration (Iftikhar et.al., 2018). The relationship between the adsorbent dosage with the adsorption capacity of Pb and the percentage of Pb removal are shown in Fig. 3 below:

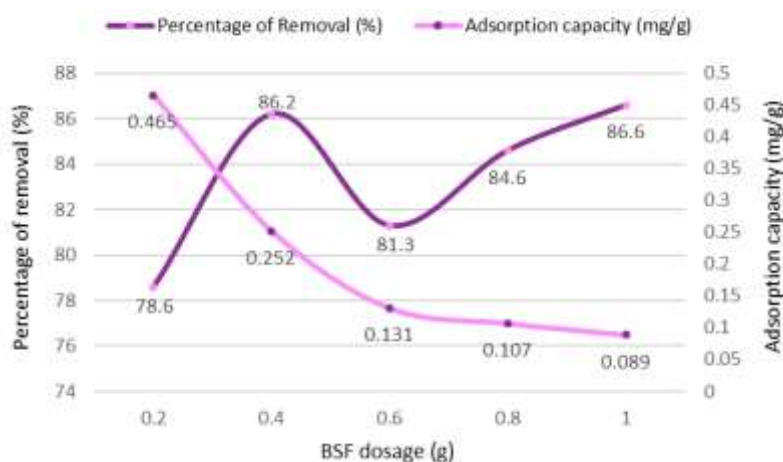


Fig. 3: The effect of adsorbent dosage on the adsorption capacity and the percentage of Pb removal

As illustrated in Figure 3, the percentage of removal increased from 78.6% to 86.2% when the adsorbent dosage was at 0.2 g to 0.4 g. Then, when the dosage increases to 0.6 g, the percentage of removal slightly decreased to 81.3%. After that, the percentage of removal starting to increase again to 84.6% (0.8 g) and 86.6 % (1.0 g). This can be explained by the fact that the greater the adsorbent mass, the larger the contact

surface area offered to Pb ions. Panda et.al, (2017) stated that increased adsorbent dosage improved the availability of additional adsorption-active sites, facilitating metal ion penetration into the adsorption sites

On the other hand, while the percentage of removal increase, but inversely the adsorption capacity decreased gradually from 0.465 mg/g to 0.089 mg/g. Ugwu et al., (2020) stipulated that as additional adsorbent is added with the same amount of Pb, this may occur since there are more binding sites available. Above 0.8 g, the amount of Pb adsorbed doesn't change. There will be a lot of un-adsorbed adsorption sites when the number of adsorption sites grows, and the concentration of heavy metals is maintained at a constant level (2.0 mg/L). Since the adsorbent capacity of 0.4 g relatively higher compared to the 1.0 g of adsorbent, 0.4 g of adsorbent was used for further adsorption parameter in this study.

Effect of initial concentration of lead

Another important factors that influence in adsorption is the initial concentration of adsorbate. The adsorption experiment was performed to study the effect of initial Pb concentration by varying it from 2.0 mg/L to 10 mg/L. The obtained experimental results are presented on Fig.4. The results indicate that with the increase in Pb concentration, the percentage of removal decreased from 89.6% to 88.45, then the percentage of removal increased to 92.5% and starting to decreased back to 92.3% and 88.4%. Meanwhile, for the adsorption capacity, it increases from 0.261 mg/g to 1.366 mg/g. Therefore, the optimum initial concentration of Pb selected for this study is 6.0 mg/L since it has high percentages of removal compared to other initial concentrations.

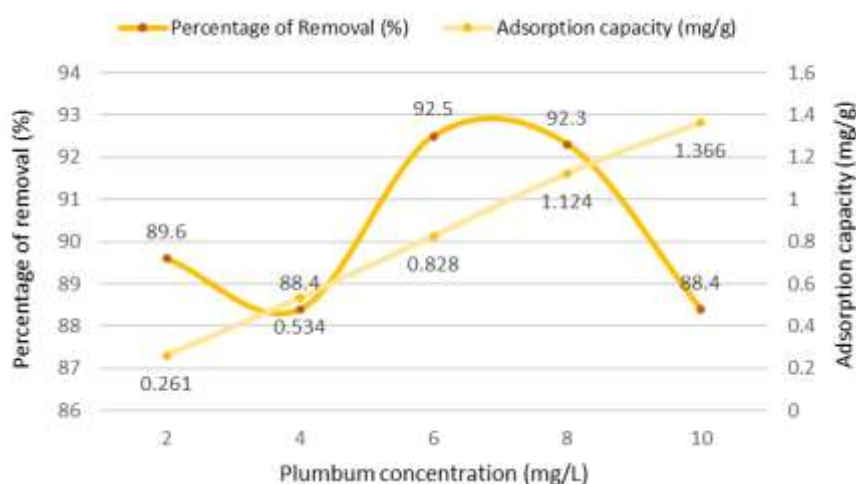


Fig. 4: The effect of Initial concentration of Pb on equilibrium adsorption capacity and removal efficiency

Boulaiche et.al., (2019) stated that this situation results from the stronger driving force provided by the concentration gradients. The equilibrium adsorption capacity of BSF increases with increasing of the Pb ion concentration, which improves the adsorption process because at higher initial concentrations, the active sites of the produced adsorbent would be surrounded by more Pb ions in the solution. Moreover, a higher metal initial concentration also results in a lower adsorption percentage. Ting et.al., (2019) stated that the ratio of empty binding sites decreased as the initial Pb concentration increased. More Pb ions were left in the solution because the adsorption site was saturated with them at a constant mass of adsorbent. Because the maximum adsorption sites were occupied at high initial metal ion concentrations, the adsorption performance is less significant.

Effect of contact time

In this stage, all of the parameters except contact time, including adsorbent dosage (0.4 g), initial Pb concentration (6.0 mg/L) and pH (11) were fixed. The effect of contact time on Pb adsorption efficiency is shown in Fig. 5 below. As it shown, the adsorption capacity is increased from 0.704 mg/g to 0.796 mg/g with the increasing of contact time from 30 minutes to 150 minutes. The plumbum uptake is comparatively a little lower in short reaction time approximately 80.7% but it increased for longer reaction time indicating that the percentage of Pb removal reached 89.3%. This indicates that at 30 minutes time, the adsorption capacity is minimal and increases slightly with increasing of the contact time to 60, 90, 120 and 150 minutes.

Panda et.al., (2017) mentioned that the uptake of metal ions happened in two stages, first with a quick uptake and then with a slower one. When there are many more accessible sites than there are metal species to be adsorbed, the adsorption process seems to move along quickly. With more metal being adsorbed, more contact time was needed. In addition, the amount of metal ions adsorbed at the time of contact reflects the adsorbent's maximum adsorption capacity under the operating circumstances (Ugwu et.al, 2020). Due to competition between the remaining BSF sites and the Pb molecules caused by the steric effect and repulsive interactions, the rate of adsorption is slowing down as there are fewer vacant adsorption sites compared to the amount of lead ions accessible (Mohd Fouzi et.al., 2018).

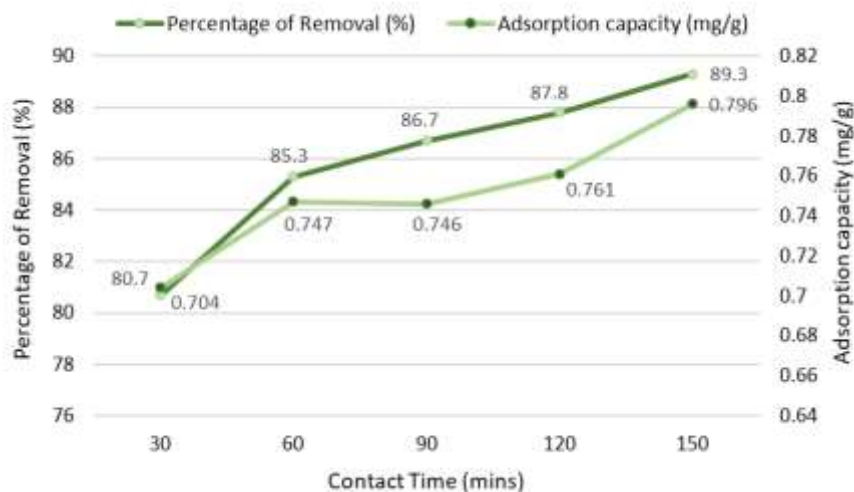


Fig. 5: The effect of contact time on Pb adsorption efficiency

4.3 Isotherm and kinetic studies

The models proposed by Freundlich, and Langmuir are the ones that are most frequently used to explain the interaction between the surface of the solid (in this study, the exoskeleton of black soldier fly) and the metal ions present in the solution (Halal et.al., 2018). Furthermore, Kajjumba et.al., (2018) stated that adsorption kinetics was evaluated to depict the rate at which a solute is retained or released at the solid-phase interface at a particular dose, temperature, flow rate, and pH for the adsorbent. This experiment used the pseudo-first-order (PFO) and pseudo-second-order (PSO), which are commonly used in practically every sorption process.

Isotherm studies

The parameter of Langmuir and Freundlich isotherm was obtained by linear regression. Table 2 provides an overview of the derived adsorption parameters and the correlation coefficient (R^2) for the examined isotherms.

Table 2: Isotherm model parameters of the adsorption of Pb onto BSF

Isotherms	Parameters	Values
Langmuir	Intercept = $1/q_{\max}$	0.77907
	Slope = $1/K_L q_{\max}$	0.12996
	q_{\max} (mg/g)	1.28358
	K_L	5.99469
	R_L	0.02273
	R^2	0.08341
Freundlich	Intercept = $\log K_f$	0.06163
	Slope = $1/n$	0.96199
	$1/n$	0.96199
	K_f (mg/g)	1.15247
	R^2	0.86919

Boulaiche et.al., (2019) mentioned that the fitness of the correlation coefficient was used to confirm the accuracy of each model (R^2). Thus, in this study, the low value of R^2 (0.08341; Table 2) indicated that the Langmuir model does not provides a good model for the adsorption system. For the Freundlich model, The greater the K_f value, the more biosorbent may be loaded. Low values of n signify high adsorption at low solution concentrations, whereas high values denote a reasonably homogenous surface. Additionally, low values of n show a high percentage of high-energy active sites (Abin-Bazaine et.al, 2022). In this experiment, the value of $1/n$ was lower than 1.0 (0.96199; Table 2), indicating that the adsorption of Pb by the exoskeleton of BSF showed a high percentage of high-energy active sites. In addition, the high value of the determination coefficient ($R^2 = 0.86919$) suggested that the Freundlich model is appropriate for describing the experimental data of the adsorption process. Hence, the adsorption of Pb using exoskeleton of BSF was taken place on the heterogenous surface of adsorbent, and multilayer Pb adsorption was possible.

Kinetic studies

The parameter of Pseudo-first-order and Pseudo-Second-Order was obtained by linear regression. Table 3 provides an overview of the derived adsorption parameters and the correlation coefficient (R^2) for the examined kinetics study.

Table 3: Kinetic modelling of Pb adsorptive uptake from aqueous solution by the exoskeleton of BSF

Kinetic	Parameters	Values
	Experimental q_e (mg/g)	0.796

Pseudo-first-order	Intercept = $\ln(q_e)$	-0.88720
	Slope = $-k_1$	-0.02438
	q_e (cal) (mg/g)	0.41181
	K_1 (min^{-1})	-0.00016
	R^2	0.72401
Pseudo-second-order	Intercept = $-1/k^2q_e^2$	3.47652
	Slope = $1/q_e$	1.26414
	q_e (cal) (mg/g)	0.79105
	q_e^2	0.62576
	K_2 (g/mg/min)	0.45967
	R^2	0.99780
	h	0.28764

The experimental adsorption data showed that the PFO model was not a good model with the correlation coefficient (R^2) value of 0.72401 for Pb. In addition, the calculated q_e (0.41181) obtained from the analysis for Pb was lower than the experimental value (0.796). This suggests that the PFO model might not be applicable to the adsorption of Pb ions onto the exoskeleton. For the PSO, The K_2 , rate constant of PSO, and initial rate of adsorption (h) were 0.45967 and 0.28764 g/mg min, respectively. The high coefficient of determination ($R^2 = 0.9978$) indicated that the PSO model is the best fit in this experimental data for Pb adsorption on the exoskeleton of BSF. Moreover, the experimental q_e (0.796 mg/g) was relatively similar to the calculated q_e (0.791 mg/g). Thus, the PSO was chosen since it has the best fit, demonstrating significant interaction between the adsorbate and the adsorbent as well as indicating the occurrence of Pb chemisorption on the surface of exoskeleton BSF.

5.0 Conclusion & Recommendations

5.1 Conclusion

In summary, the exoskeleton of BSF can be effectively used as a low-cost for Pb removal from an aqueous solution. With the maximum adsorption capacities of Pb found to be 1.1525 mg/g and the removal efficiencies obtained relatively high which is between (60 -100%). It has been confirmed that the process of Pb adsorption by BSF is dependent on the pH of the solution, adsorbent dosage, initial Pb concentration and the contact time. The isotherm and kinetic study indicate that the monolayer adsorption happens and chemisorption of Pb could probably take place onto the heterogeneous of available active sites of the exoskeleton of BSF.

5.2 Recommendations

There are some aspects and area in the utilization of the exoskeleton of BSF as heavy metal adsorbents that can be studied in the future:

- Extraction of the exoskeleton of BSF for better adsorption efficiency
- Study of adsorption at other parameters such as other type of heavy metals, temperature, mixed samples or wastewater from industry
- Creation of ecological friendly scaffold for the adsorbent

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Paper Contribution to Related Field of Study

This study explores the potential of BSF exoskeleton or chitin from BSF in removing heavy metal.

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