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Use of Low-Cost Adsorbent for Copper and Lead Removal from Aqueous Solutions

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ABSTRACT

In this study, the effect of the use of environmentally friendly materials (sawdust) in the reduction of some heavy elements of industrial wastewater was studied. The removal of lead and copper elements was tested. In order to evaluate the effect of this material and other factors in increasing the efficiency of removal, different concentrations of heavy elements of lead and copper 5, 10, 15, and 20 mg/l and contact time (10, 20, 30, and 40 s) were tested. The effect of pH was also investigated at levels of (3, 5, 7, and 10, as well as the impact of the amount of sawdust used and the rate of speed of mixing was 75, 100, 150, and 250 rpm. The results showed that the highest lead removal efficiency was (95%) when using 2 gm of sawdust at ten pH. In comparison, the highest removal efficiency of copper was 92.5%, when the pH 7 and the study of the number of revolutions and contact time. The results were good indicators when the value of the agitation speed was 75 rpm. Lead removal was 98%, and copper was 94.5% at a speed of 100 rpm. The result also recorded significant effect of time on the removal efficiency; the efficiency of removal of copper was 90–94% at 30 min, while the removal efficiency of lead was 70–73% at 34–40 minute period.

Keywords: environmentally friendly material, heavy elements, industrial water, contact time.

INTRODUCTION

Water pollution with heavy metals has become a common environmental problem. Rivers and groundwater are often contaminated with heavy metals from various sources, which may be natural, resulting from atmospheric effects on rocks and soil, or human sources, resulting from the improper disposal of industrial waste by factories in gaseous, liquid, or solid form, which settles in the terrestrial environment and finds its way into the aquatic environment (Rainbow 2002; Kalash et al. 2020). Heavy metals are defined as elements with atomic weights exceeding 100 and densities exceeding 5 g/cm^3, including zinc, cadmium, copper, lead, mercury, chromium, and others (Srivastava and Majumder 2008). Their danger lies in their transitional nature. Some of these elements are essential, such as iron, copper, and zinc, as living organisms require small amounts of them, but they become toxic when they exceed the recommended limits. Other elements, such as cadmium, lead, mercury, and silver, are non-essential and toxic even at relatively low concentrations (Naseem and Tahir 2001). Most organic waste and heavy metals are not biodegradable by bacteria and other natural processes, and their persistence enables them to spread over long distances from their sources. The most dangerous aspect of heavy metals is their ability to bioaccumulate in the tissues and organs of various living organisms, causing physical disorders and damage. There are several traditional and common methods for removing heavy metals from water, such as chemical precipitation, ion exchange, membrane filtration, reverse osmosis, electrodialysis, and activated carbon adsorption, among other costly methods (Chaudhari and Tare 2008). Research and studies have focused on sustainable methods using environmentally friendly techniques as long as they are effective, low-cost, and easy to apply and implement. Biochemical, chemical, and physical sorption are alternative methods to traditional methods that are highly effective in removing heavy metals from aqueous solutions (Namasivayam and Ranganathan 1998). They are considered low-cost because they use readily available materials in the environment, such as agricultural and plant waste, such as rice and wheat husks, sawdust, and fibers (Arora 2019). These materials can be used directly or after activation with certain chemicals added to the waste of these plants, such as organic acids, bases, oxidizing agents, and organic compounds, to improve the absorption properties, such as increasing removal efficiency and effectiveness (Kadhom et al. 2020). If these agricultural waste products are not treated and activated and used directly in heavy metal sorption processes, some problems may arise, such as reduced sorption efficiency and increased chemical and biological oxygen demand (COD, BOD) requirements, as well as an increase in total organic compounds, which can cause oxygen depletion in water, threatening aquatic life (Gaballah et al. 1997).

The efficiency of using sawdust obtained from wood factories at low prices to remove copper and chromium ions was studied by Sciban et al. (2006). Two types of sawdust (poplar and firewood) were treated with sodium hydroxide and sodium carbonate solutions, and their adsorption capacity was compared to untreated sawdust. It was observed that untreated sawdust in both types showed high adsorption capacity for copper ions, higher than for chromium ions (Sćiban, Klasnja, and Skrbić 2006). After treatment with sodium hydroxide solution, an increase in the adsorption capacity for both copper and chromium ions was observed, with the capacity being 2.5 times higher for copper and 15 times higher for chromium compared to untreated sawdust. The adsorption capacity for copper and chromium ions was calculated using the Langmuir model, and it was found to be 12.7 mg/g for fir sawdust and 6.92 mg/g for poplar sawdust for copper ions, while for chromium ions it was 13.4 mg/g for fir sawdust and 15.83 mg/g for poplar sawdust.

The effect of sulfuric acid treatment on sawdust was studied by Acar and Eren (2006), and it was found to be effective in removing 92.4% of copper ions at a pH of five, while untreated sawdust removed 47% of copper ions. It was found that 70-80% of copper ions were removed from the solution within ten minutes. The adsorption capacity was found to be higher when sawdust was treated with sulfuric acid compared to sodium hydroxide solution treatment (Acar and Eren 2006). The use of rice husks for heavy metal removal was extensively reviewed by Chuah et al. (2005), including elements such as cadmium, lead, chromium, copper, cobalt, nickel, and gold (Chuah et al. 2005). Rice husks can be used to treat both treated and untreated heavy metals, and on the whole, chemical treatments of rice husks showed higher adsorption capacity for heavy metals than untreated husks. For example, Kumar and Bandyopadhyay (2006) reviewed rice husks treated with hydraulic acid (Kumar and Bandyopadhyay 2006) and sodium hydroxide solution, while Guo et al. (2003) reviewed rice husks treated with sodium carbonate solution (Guo et al. 2003). Kumar and Bandyopadyay (2006) found that the addition of sodium hydroxide increased the adsorption capacity for cadmium, as it removes the soluble minerals from the surface of rice husks that impede the adsorption process. Tarley et al. (2004) found that the adsorption of cadmium increased approximately twofold when rice husks were treated with sodium hydroxide solution, with the adsorption capacity being 7 mg/g for treated rice husks and 4 mg/g for untreated rice husks (Teixeira Tarley, Costa Ferreira, and Zezzi Arruda 2004).

In this paper, sawdust powder was used as an adsorbent for removing Cu and Pb ions from wastewater. The sawdust powder was then treated with sodium hydroxide solution and used for the adsorption process. Different operating conditions were studied, including adsorbent dose, reaction time, pH of the solution, and agitation speed.

METHODS

Wood shavings were prepared after washing them with distilled water several times to remove impurities and drying them in a drying oven at a temperature of 100°C for 24 hours to increase the surface area. A portion of these shavings was taken and treated with a solution of sodium hydroxide and dried in the drying oven again for use in experiments. Two grams of the wood shavings treated with sodium hydroxide were taken for lead and copper, respectively, and four samples were taken for each element, along with untreated samples for each element, to conduct experiments on them. Standard solutions were prepared with concentrations of (5, 10, 15, 20) mg/L for lead and copper, and these solutions were mixed with the wood shavings treated and untreated with sodium hydroxide and placed in a shaking incubator at a frequency of 150 cycles/minute and a temperature of 37°C for ten minutes. The samples were then filtered using filter paper to obtain a clear and precipitate-free solution, which was analyzed using an atomic absorption spectrophotometer to record readings and calculate the removal percentage for both lead and copper, as shown in Figure (1). A second experiment was conducted to calculate the removal efficiency for the same two elements by taking different weights (0.5, 2, 3.5, 5) grams of wood shavings, four samples for lead treatment, and four untreated, and the same samples were taken for copper. They were mixed with a standard solution of 2 mg/L concentration for both lead and copper, and the samples were placed in a shaking incubator at a frequency of 150 cycles/minute and a temperature of 37°C for ten minutes. The samples were then filtered using filter paper to obtain a clear and precipitate-free solution, which was analyzed using an atomic absorption spectrophotometer to record readings and calculate the removal percentage for both lead and copper, as shown in Figure 2. The removal percentage for both lead and copper was then calculated using different readings of the acidic function, where a standard solution was taken with a concentration of 2 mg/L for both lead and copper to conduct experiments on them, and the acidic function was adjusted for the samples, with values of 3, 5, 7, and 10, respectively. These solutions were mixed with 2 grams of wood shavings, and the samples were placed in a shaking incubator at a frequency of 150 cycles/minute and a temperature of 37°C for thirty minutes. The samples were then filtered using filter paper to obtain a clear and precipitate-free solution, which was analyzed using an atomic absorption spectrophotometer to record readings, as shown in Figure 3. Using the same steps as the previous experiments, the removal percentage for copper and lead was calculated using different exposure times (10, 20, 30, 40) minutes when the samples were exposed to the vibrating device, as shown in Figure 4. The removal percentage for both lead and copper was also calculated using the same steps as the previous experiments, with a change in the number of cycles in the shaking incubator (75, 100, 150, 200) per minute for a duration of 20 minutes, as shown in Figure 5. The removal efficiency for both lead and copper was calculated using the following equation:

$$Removal\ (\%) = \frac{C_i - C_f}{C_i} \quad (1)$$

where: C_i – the initial concentration of the heavy metal, C_f – the final concentration.

RESULTS AND DISCUSSION

Several experiments were conducted using different variables to study their effect on the efficiency of lead and copper removal by sawdust in order to achieve the highest removal efficiency. When testing the impact of heavy metals in water, it was observed that an increase in concentration had a negative effect on removal efficiency.

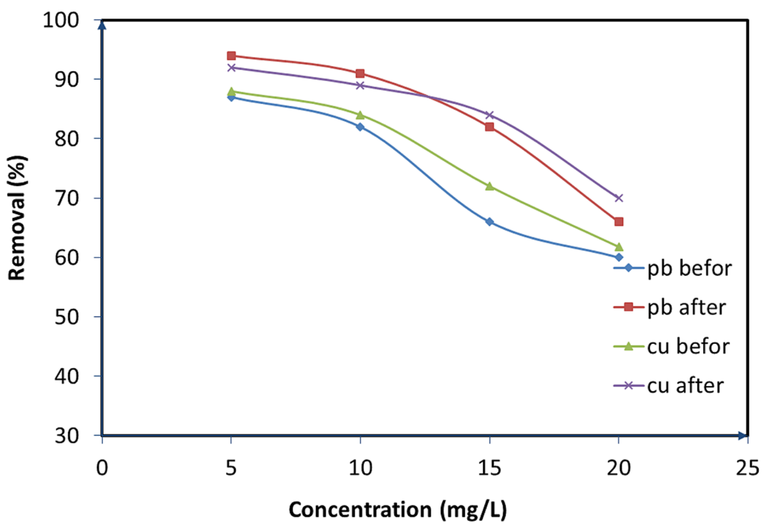

Figure 1. The effect of Pb and Cu concentrations on the removal ratio

Figure 1 shows that the removal efficiency of lead reached 51.3% at a concentration of 15 mg/L, while it decreased to 36.5% at a concentration of 20 mg/L. As for copper, the removal efficiency reached 62.2% at a concentration of 15 mg/L and decreased to 61.8% at a concentration of 20 mg/L. When treating sawdust with a sodium hydroxide solution, it was observed that the removal efficiency of lead increased to 88.6% at a concentration of 15 mg/L and also decreased to 66% at a concentration of 20 mg/L. In the case of copper, the removal efficiency increased to 84% at a concentration of 15 mg/L and decreased to 82% at a concentration of 20 mg/L. From the previous two experiments, it can be concluded that the removal efficiency of lead is higher than that of copper after treatment. Similar findings were reported by other researchers (Yu et al. 2000).

To study the effect of the weight of sawdust on the removal efficiency of lead, the best removal was observed at a weight of 3.5 grams, reaching 84%, and decreased to 80% at a weight of 5 grams. Meanwhile, the removal efficiency of copper was 77.5% at a weight of 3.5 grams and increased to 85.5% when using 5 grams of sawdust. When treating sawdust with a sodium hydroxide solution, the removal efficiency of lead increased to 97% at a weight of 3.5 grams and decreased to 95% at a weight of 5 grams. As for copper, the removal efficiency was 83% at a weight of 3.5 grams and increased to 90.5% at a weight of 5 grams. The presence of sawdust as a media at weights greater than 5 grams leads to an increase in solid and colloidal suspended matter, which affects the purification process by causing filter clogging and increasing waste materials (Meez, Rahdar, and Kyzas 2021).

Figure 2 shows the effect of different weights of sawdust on the removal efficiency of lead and copper. The acidic function has a significant impact on the removal process, where the highest removal percentage for lead was 95.5% at pH 10, while the lowest removal percentage was 75% at pH 3. The removal percentage for copper was 92.5% at pH 7 and 87.5% at pH 3. At high acidic function values, water solubility decreases, and heavy metals become easy to remove and tend to precipitate and separate from water, moving towards the adsorbent material. Thus, their concentration in water decreases. Additionally, the precipitation or separation of heavy metals depends on their concentration in water, in addition to their acidic function. An increase in the acidic function value means an increase in the concentration of the negatively charged hydroxide ion, which tends to react with the positively charged soluble heavy metals, forming the non-soluble metal hydroxide, making it easy to separate by precipitation. Therefore, the reason for the increase in the removal percentage at high pH values is due to precipitation and adsorption. Each heavy metal has different solubility at different pH values (Rainbow 2002), but most heavy metals tend to precipitate at acidic function values greater than 7.5, as shown in Figure 3. Similar results were reported by other papers (Meez, Rahdar, and Kyzas 2021).

Figure 4 illustrates the effect of contact time on the removal percentage, where the highest removal for the lead was 73% after 40 minutes of adding the adsorbent material. We notice that this percentage decreases with prolonged contact time due to the adsorption capacity of the material with lead. On the other hand, the removal percentage of copper was 96% at a contact time of 30 minutes, and this percentage decreased relatively with longer times due to the material's saturation and the solubility of copper in the solution if it stays for more than 30 minutes in the solution (Megat Hana et al. 2007).

The removal percentage is affected by several conditions, in addition to the nature of the chemical and physical solution, as it is influenced by external factors such as mixing speed, the number of cycles, contact speed, and the interaction between the added materials and the solution containing heavy metals, which facilitates the transfer of ions from the solution to the adsorption medium, leading to an increase in the efficiency of heavy metal removal by increasing the number of cycles per minute. The highest removal percentage for lead was 98.5% when the solution was exposed to 75 cycles/minute in a shaking incubator, while the highest removal percentage for copper was 94.5% at a rotation speed of 100 cycles/minute, as shown in Figure 5. Furthermore, increasing the number of cycles beyond the required limit leads to opposite results due to the stresses generated by the cycle speed, which creates a centrifugal force for the adsorbed ions, causing them to dissolve again in the solution. Additionally, the high mixing speed does not allow for proper contact between the pollutants (heavy metals) and the added material (Namasivayam and Ranganathan 1998).

The isotherm study was conducted under the optimum operating conditions to understand the adsorption mechanism. There are two standard adsorption isotherms that are typically studied:

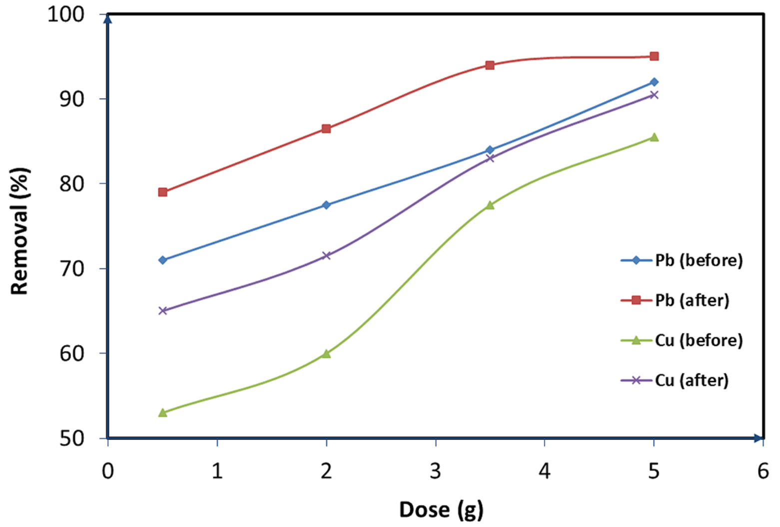

Figure 2. Effect of the adsorbent dose on the removal ratio of Pb and Cu

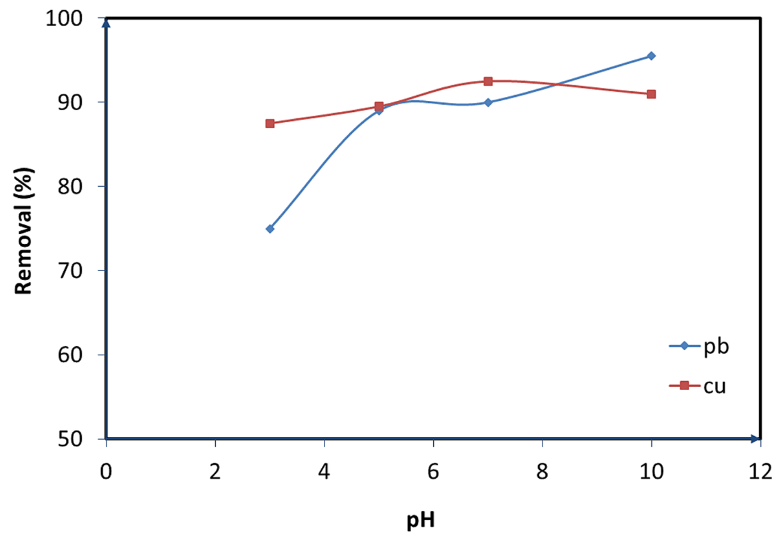

Figure 3. The effect of pH on the removal ratio of Cu and Pb

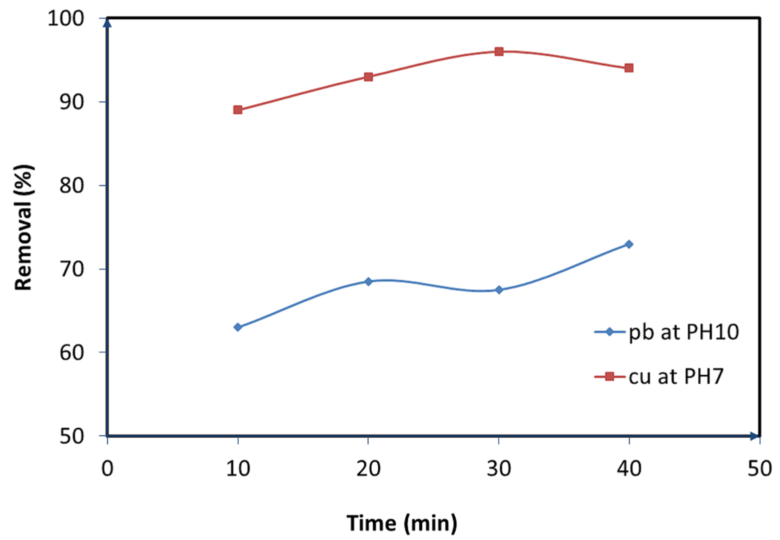

Figure 4. Effect of the adsorption time on the removal ratio of Cu and Pb

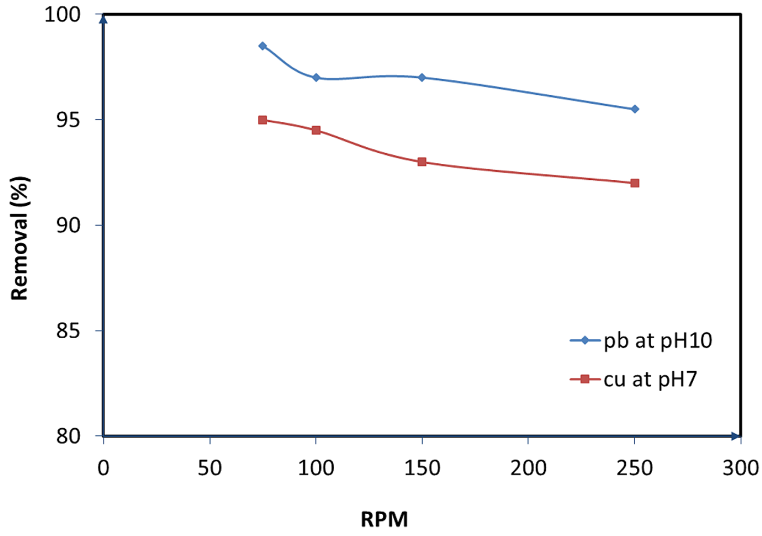

Figure 5. Effect of the agitation speed on the removal ratio of Cu and Pb

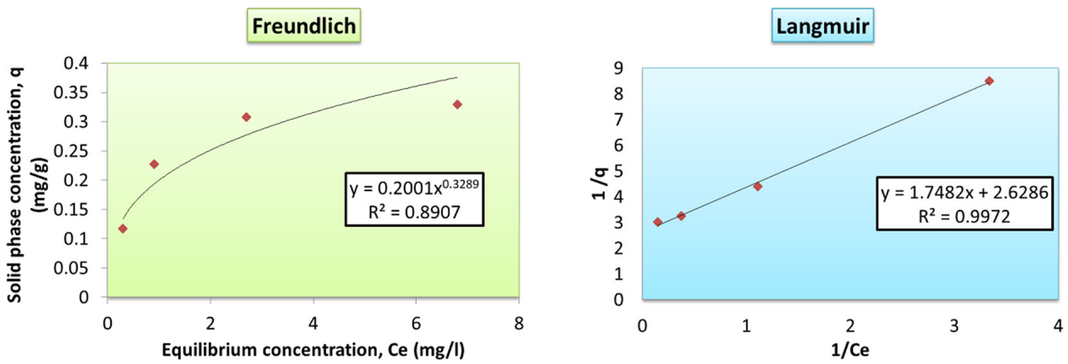

Figure 6. The adsorption isotherm models of Pb adsorption on sawdust particles

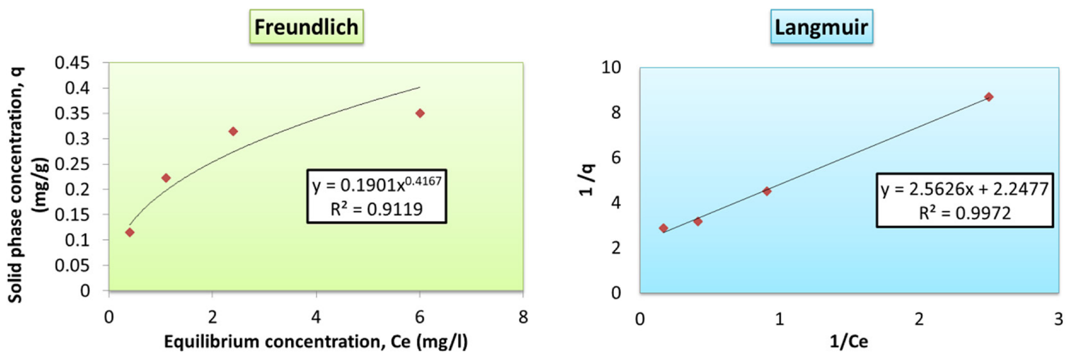

Figure 7. The adsorption isotherm models of Cu adsorption on sawdust particles

Freundlich and Langmuir models. More details on the calculations of these models can be found elsewhere (Kadhom, Kalash, and Al-Furaiji 2021; Kalash et al. 2020). Freundlich isotherm agrees with the heterogeneous adsorption that occurs in the form of multilayers. It assumes that when the adsorbate concentration increases, the adsorption uptake increases (Khairi R. Kalash and Mustafa Al-Furaiji 2020). Langmuir isotherm describes the dominant adsorption that occurs in a single-layer adsorbent's structure; it adopts the formation of a homogeneous monolayer with limited adsorption capability. When the adsorbate particles fill the adsorption spots, no more molecules can be adsorbed on these sites(Alalwan and Alminshid 2020). Figures 6 and 7 show the adsorption isotherms for both Pb and Cu adsorption, respectively. It can be seen from the Figures that the adsorption of both heavy metal ions was a better fit with the Langmuir model. This can be concluded from the R^2 values where the highest coefficient values were found in the Langmuir isotherm (R^2 = 0.9972). This finding assumes that the adsorption of Pb and Cu ions on the sawdust particles occurred in a physical homogenous monolayer process.

CONCLUSIONS

Treating sawdust with a sodium hydroxide solution increases the efficiency of lead and copper removal due to an increase in adsorption capacity through increased sawdust porosity. Using more than 5 grams of sawdust leads to an increase in impurities, which affects the purification process by clogging filters and increasing waste materials. An alkaline environment above 7.5 helps increase the concentration of negative OH- ions, which tend to react with positively charged heavy elements to form insoluble hydroxides. The efficiency of heavy metal removal is achieved if they remain in contact with sawdust for a long period due to sawdust saturation. Increasing the number of cycles and mixing speed per minute leads to opposite results, as the removal efficiency decreases due to the contact between the precipitate and the element being rapid. In addition, high speed generates stress that causes the ions to return to the solution and dissolve again.

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