



### Arsenic Removal from Aqueous Solutions by Raw and Incinerated Pine Bark

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#### Abstract

In this research, raw and incinerated pine barks were evaluated as absorbents for the removal of pentavalent arsenic As(V), from aqueous solutions. After preparing artificial wastewater samples containing different concentrations of arsenic, the impact of the parameters including pH, adsorbent dosage, contact time and initial arsenic concentration was assessed on arsenate adsorption level by both of the absorbents. The results showed that the pine bark ash could remove arsenic from aqueous solutions better than the raw pine bark in optimum conditions of contact time of 60 minutes, pH 7, adsorbent dosage of 1 g/l and initial arsenic concentration of 1000 µg/l with absorption efficiency of 95.86%. Considering the high efficiency of absorbent at neutral pH as well as the availability and low cost of the pine barks, the use of pine bark ash is suggested as an effective absorbent for removing arsenic from aqueous solutions.

**Keywords:** *Pine Bark, Arsenic, Aqueous Solutions.*

#### Introduction

Arsenic (As) is a trace element in the Earth's crust. Arsenic ranks twentieth in abundance of elements in the earth's crust, fourteenth in seawater and is the twelfth most abundant element in the human body (1).

This metalloid is known as one of the most toxic and carcinogenic chemical component. Many people around the world have been poisoned by arsenic, which is the greatest history of poisoning in the world (2, 3).

Scientists believe that arsenic is found in large quantities in soils, rocks and sedimentary deposits that are imported into surface water and groundwater through erosion, dissolution and microbial reactions (4, 5).

Artificial sources of arsenic contamination in soil and water systems generally include mining activities, discharge of industrial wastes, agricultural uses, oil refineries and burning of fossil fuels as well as metal, glass and ceramic industrials wastewaters (6, 7). Drinking water is as a significant source for heavy metal or another form of pollutants such as arsenic exposure (8-12).

Arsenic in natural water is available in two forms: arsenate As(V) and arsenide As (III), both of which are toxic to humans and plants. The As(V) is the predominant form of Arsenic in surface waters, while the As (III) can be seen more in groundwater. Arsenic enters to the water resources through the dissolution of minerals, industrial wastewater discharge and atmospheric accumulation (13).

Epidemiological studies have shown that increased prevalence of human cancers such as in skin, lung, liver, kidney and bladder is associated with the presence of arsenic in foods and drinks (14, 15). Inorganic arsenic is always considered as carcinogens for human and is a factor in increasing the risk of cancers in skin, nasal cavity, lung, bladder, colon, liver and kidneys (16).

According to the Iranian National Standards Organization, the maximum contaminant level (MCL) for arsenic in drinking water is 0.05 mg/L (17). The US Environmental Protection Agency (USEPA) has reported the arsenic drinking water standard about 5 to 10 µg/l (18). The guideline of WHO for arsenic is 0.01 mg/L (19). There are several methods with different advantages and disadvantages to removal pollutants such as arsenic and reduce it to the limits in drinking water, including coagulation, filtration, activated alumina, ion exchanges and membranous processes (20- 24).

Adsorption process is the best method to remove arsenic due to easy transportation,

no sludge exploitation, no need to add chemicals, removal of multiple contaminants with high efficiency and the use of acidic and alkaline leachate to revive absorbent (25). Several studies have ever been conducted on the use of agricultural wastes and pine bark in order to adsorb various contaminants from aqueous solutions (26- 29). Therefore, this study was conducted to examine the efficacy of pine bark ash to remove arsenic from aqueous solutions by adsorption process.

## Materials and Methods

In the present in vitro experimental research, initially certain concentrations of arsenic (100, 1000 and 2000 mg/l) were prepared in a batch reactor. Then the effect of factors influencing the process including pH (3, 5, 7, 9 and 11), contact time (0 to 120 minutes) and adsorbent dosage (0.5, 1, 1.5 and 2 g) were analyzed separately on removal efficiency (at a temperature of 25 °C). All chemicals used in this survey including sodium arsenate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ) were prepared from reputable company of Merck, Germany.

The artificial wastewater samples soaked in required amounts of arsenic were produced by dilution and were used on a daily basis. In this research, the two absorbents were pine bark ash and raw pine bark. To prepare absorbents, first pine tree bark was washed with distilled water several times to remove dust and other impurities. The samples were dried in an oven at 105°C for 24 hours and turned to ash by using an electric furnace at 600°C for 2 hours. After preparing the ashes, the samples were placed in desiccator until use to avoid weight changes.

The pH of samples was adjusted by hydrochloric acid and 0.1M sodium hydroxide, respectively, from 3 to 11. After the processing, the samples were removed from the process in due time and filtered by Whatman filter paper (0.45 micron). Changes in arsenic concentrations were determined by silver diethyl dithiocarbamate according to the Standard Method 3500-As using UV-VIS spectrophotometer at a wavelength of 520 nm (30).

All experiments were repeated twice to increase the accuracy of the tests, and finally the results were reported based on mean. The removal efficiency was calculated using Equation 1.

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

Where,  $C_0$  initial concentration of arsenate in solution, and  $C_e$  final concentration of arsenate in solution.

## Results and Discussion

### The Effect of pH

The pH of aqueous solution is a very important parameter in the adsorption process. Metal ion binding occurs by surface groups strongly dependent on the pH. The effect of pH on arsenate removal efficiency was investigated by changing the initial pH of the samples (3, 5, 7, 9 and 11), and in stationary conditions of initial arsenic concentration of 100 µg/l, fixed amount of adsorbent of 0.5 g/100 ml for all samples for 30 minutes.

Finally, the remaining arsenate concentrations were determined. Figure 1 indicates the percentage of arsenate removal using raw pine bark and pine bark ash at different pH. According to the results, absorption efficiency elevated with increasing pH from 3 to 7 for the ash and from 3 to 5 for the raw bark and declined with further increase in pH for both of the adsorbents.

The high removal rates were seen in the range of pH 3 to 7 for both of the adsorbents so that the maximum removal rates were 96.59% for ash at pH 7 and 83.22% for raw bark at pH 5. There are various forms of arsenic ions at different pH.

In fact, arsenate pH < 3 is found mainly in the form of  $H_3AsO_4$ . The non-ionic form has no reluctant to electrostatic attraction. Moreover, reducing the pH of the solution leads to an increase in positively charged groups on the surface of the adsorbent and in electrostatic repulsion between metal ions and positively charged groups on the absorption surface.

According to the results of other researchers, arsenate is very active in the pH 4 to 9 as well as ready to remove via various ways including adsorption process. On the other hand, the charge on the surface of the adsorbent is negative at high pH, reducing the reluctance of anions attraction through electrostatic process (31-32).

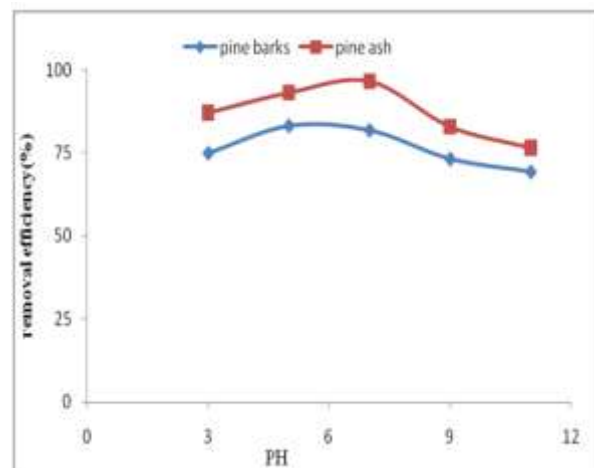


Fig 1: Effect of PH on the removal of arsenate by pine barks and ash

### The Effect of Adsorbent Dosage on the Arsenate Removal

The effect of adsorbent dosage on the removal efficiency was measured with changes in adsorbent concentrations (0.5, 1, 1.5 and 2 g/L), in stationary conditions of initial arsenic concentration of 100 µg/l and contact time of 30 minutes using the optimal pH separately for ash (7) and raw bark (5).

The remaining arsenate concentrations were determined after adsorption process. As can be seen from Figure 2, arsenate removal rate showed significant increase by rising adsorbent dosage from 0.5 to 1.5 g/L for ash and raw bark.

This increase is due to the high active absorption sites on adsorbent that can be offered to arsenate ions with increasing adsorbent dosage. Nevertheless, there is no significant change in arsenate removal with further increase in adsorbent dosage from 1.5 to 2 g/L. In fact, with more elevation in adsorbent dosage, many unsaturated adsorption sites will remain on the adsorbent because of the limited number of arsenate ions in solution (33).

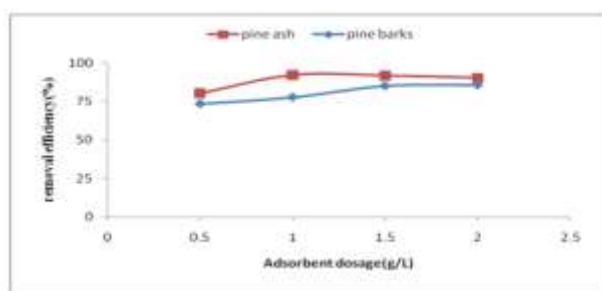


Fig 2: Effect of Adsorbent dose (g/L) on the removal of arsenate by pine barks and ash

### The Effect of Contact Time on the Arsenate Removal

The effect of contact time on removal efficiency was detected by changing the contact time of the samples (30, 60, 90 and 120 min), in the amount of 1 g adsorbent and the optimum pH of 7 for ash samples and in the amount of 2 g adsorbent and optimum pH of 5 for raw bark in stationary conditions of initial arsenic concentration of 100  $\mu\text{g/l}$  for all samples.

The remaining arsenate concentrations were measured after adsorption process. As Figure 3 shows, the removal efficiency improves from 75.18 percent to 93.77 percent when the contact time is elevated from 30 minutes to 120 minutes in the ash samples; but arsenate removal efficiency remained almost stable by rising the contact time up to 120 minutes. So, time to reach balance in pine ash was obtained 60 minutes. In addition, when the contact time lasted from 30 minutes to 120 minutes in raw bark, the removal efficiency promoted from 42.62 percent to 84.11 percent. Therefore, time finding balance in raw bark was 120 minutes.

The adsorption levels are rapid at first; after this stage, the removal rate enhanced with prolonging contact time and before reaching balance. The rapid absorption occurs due to passive absorption as physical adsorption or ion exchange on the surface of the adsorbent.

On the other hand, since the active absorption sites on the adsorbent are certain in number and each active site is able to attract only one ion in single-layer system, so metal absorption through the adsorbent is fast at the beginning. However, the available active sites decrease with time, resulting in

reduced absorption rates due to competition of metal ions remaining in the solution to absorb on the sites (34).

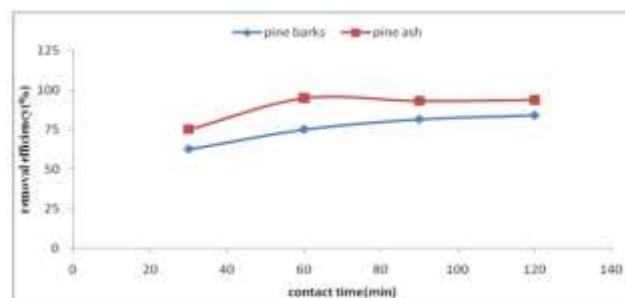


Fig 3: Effect of Time (min) on the removal of arsenate by pine barks and ash

### The Effect of Initial arsenic Concentration on Removal Efficiency

The effect of initial arsenic concentration on removal efficiency was investigated by changing the initial arsenic concentration from 100 to 2000  $\mu\text{g/l}$ , at pH 7, 1 g adsorbent and contact time of 60 minutes for pine ash; as well as at pH 5, 2 g adsorbent and contact time of 120 minutes for raw bark. In accordance with Figure 4, on both of the diagrams, promoted initial concentration of metal firstly leads to an increase in metal removal rates up to a concentration of 1000  $\mu\text{g/l}$ , but then the removal efficiency decreases with further increase in initial concentration of the metal.

The reason for this is the limited active sites on the surface of adsorbent, which these exchangeable sites in the absorption structure are saturated by raising the initial concentration of metal in solution, thereby reduced removal rate (35). In a study conducted by Mehrasbi et al. on banana bark, they concluded that absorption efficiency increases at first and then decreases with improving initial concentration of metal ions (17).

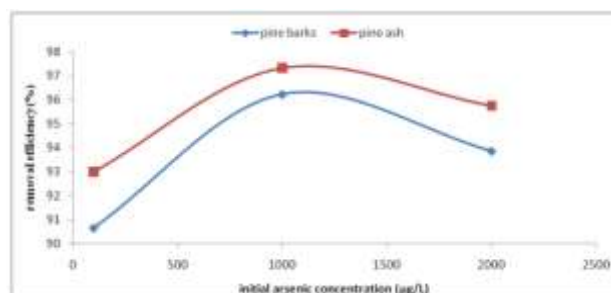


Fig 4: Effect of initial arsenic concentration ( $\mu\text{g/L}$ ) on the removal of arsenate by pine barks and ash

## Conclusion

The experiments demonstrated that the pine bark ash is more efficient in arsenate removal compared to the raw pine bark. The optimum pH values for removal of arsenate were 7 and 5 to pine ash and raw bark, respectively. Given that the pH of 7 is approximately close to the pH of natural waters and optimization is not required when using absorbent, this will reduce the cost of system administration. The optimum contact time for removal of contaminants in the pine ash was about an hour less than the raw bark.

In addition, the optimum adsorbent dosage was 1 g/L and 2 g/L in the pine ash and raw bark, respectively. Hence, the pine tree bark can be applied as a promising approach for removing arsenic from aqueous solutions due to the low cost, its abundance in the region, less contact time and adsorbent dosage, no need to adjust the pH and the ability of arsenate removal by using the ash.

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