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Removal of Arsenic Ions from Aqueous Solution with Different Activated Stems

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Abstract:
Environmental pollution is one of the most serious problems we are facing today. The indispensability, deficiency or toxicity of arsenic is manifestation of dosage response effects blood is also a good indicator for presence of arsenic in human body. The objective of this study was to study the arsenic adsorption behaviour on activated stem ash of Salvadora Persica and Azadrichta Indica Batch studies were conducted using these adsorbents with aqueous solution different concentrations (0-500 μg/L) of arsenic. The adsorption capacity of the Salvadora Persica and Azadrichta Indica used in this study for arsenic was estimated as 92% and 86% respectively. The experimental data fitted well with the well-known isotherms namely Freunlich and Langmuir indicating a favourable adsorption by these adsorbents.

***Keywords**: Azadrichta indica, Arsenic, Freunlich isotherm, Langmuir isotherm, Salvadora persica*

1. Introduction

Water plays a vital role in human life. Natural resources are important wealth of our country water is one of them. Water is a wander of the nature. "No life without water '' is a common saying depending upon the fact that water is the one of the naturally occurring essential requirement of all life supporting activities Since it is a dynamic system, containing living as well as nonliving, organic, inorganic, soluble as well as insoluble substances. So its quality is likely to change day by day and from source to source. Any change in the natural quality may disturb the equilibrium system and would become unfit for designated uses. (Murheka 2012)

2. Materials

2.1. Adsorbent Used

The stem of Azadirachta indica (Neem) and Salvadora persica are used as natural adsorbents. Azadirachta indica and Salvadora persica is commonly available all parts of India. These adsorbents are collected from commercial saw mills.

2.2. Water

Distilled water was obtained by distilling tap water in glass distillation apparatus. All the working arsenic solutions were prepared in freshly prepared double distilled water unless otherwise mentioned. The pH of the distilled water was around 6.9.

2.3. Instrumentations

- UV-VisibleSpectrophotometer: Model no: DR 2700Wavelength: 530nm
- High Precision Digital Balance
- Digital pH Meter
- Magnetic Stirrer

3. Methodology

3.1. Preparation of Adsorbent

The stem of Azadirachta indica (Neem) and Salvadora persica were taken from commercial saw mill source. These materials were firstly washed with distilled water to remove impurity such as sand, leaves and soluble and colored components dried at 100^0C for 12 hours, burned at 300^0C for 30 min, crushed in a domestic grinder and sieved to obtain a particle size in the range of 5 to 90 mm (mean size for higher efficiency). The powdered adsorbent stored in an airtight container until use. No other chemical or physical treatments used prior to adsorption experiments.

3.2. Preparation of Arsenic Aqueous Solution

3.2.1. Arsenic Standard Stock Solution

All the chemicals used were of analytical grade. Weigh exactly 133 g of arsenic trioxide, previously very finely powdered and dried at 105^0C for 4 hours and dissolve it in 5 ml of sodium hydroxide solution (1/ 5). Neutralize with diluted sulfuric acid (1/ 20) and add 10 ml of diluted sulfuric acid (1 /20) and freshly boiled and cooled water to make exactly 1000 ml. One ml of this solution contains 0.5 mg or 500 µg of arsenic trioxide (As_2O_3). The stock solutions are prepared based on the standards methods mentioned in Alpha (2005).

pH	Adsorbent dosage (g/L)	Salvadora persica and Azadrichta indica stem ash (∘C)	Arsenic concentration, µg/L	Contact time, Min
2, 4, 6, 7, 8, 9, 10, 11	0.5, 1.5, 2.5, 3, 5, 6	300	10, 50, 100, 150, 200,300, 400, 500	20, 40, 60, 80, 100, 120, 180, 240

Table 1: The Ranges Of Experimental Parameters.

3.2.2. Arsenic Standard Solution

Measure exactly 10 ml of Arsenic Standard Stock Solution, add 10 ml of diluted sulfuric acid (1/ 20) and add freshly boiled and cooled water to make exactly 1000 ml. One ml of this solution contains 25 µg of arsenic trioxide (As_2O_3). Prepare freshly before use and store in a bottle with a ground-glass stopper.

3.3. Batch Adsorption Experiments

3.3.1. Effect Of Salvadora Persica And Azadirachta Indica Stem Ash Dosage.

Batch adsorption experiments were done at a different Salvadora persica and Azadirachta indica stem ash (obtained at 300^0C) concentration from 0.5 g to 6 g in a 100 mL solution of 300µg/l of As(III) at pH 6.0, for a contact time of 80 min at 26 ± 2^0C. Flasks will be agitated on a magnetic stirrer at 100 rpm the mixtures were then filtered through whatman 42 filter paper and the concentration of As(III) in the filtrates will be analyzed using a spectrophotometer. The above procedure was repeated three times and the average value will be taken.

3.3.2. Effect Of Solution pH On As(Iii) Adsorption.

The effect of solution pH on the adsorption capacity of Salvadora persica and Azadirachta indica stem ash (3 g) obtained at 300^0C was investigated using a 100 mL solution of 300µg/l of As(III) for a pH range of 2 to 11 at 26±2^0C. The samples were then agitated and filtered and the filtrates will be analyzed as mentioned before.

3.3.3. Effect Of Contact Time.

Batch adsorption experiments were carried out at different contact times (20, 40, 60, 80, 100, 120, 180, 240 min) for an initial concentration of 300µg/L of As(III) solution at pH 6.0. The Salvadora persica and Azadirachta indica stem ash (obtained at 300^0C) dose was 3.5 g in 100 mL solution in 250 ml conical flask at 26 ± 2^0C. The samples were then agitated and filtered. The filtrates were analyzed as mentioned before.

3.3.4. Effect Of Initial As (III) Concentration.

Batch experiments were carried out by contacting 3 g of Salvadora persica and Azadirachta indica stem ash (obtained at 300^0C) with 500 mL of As(III) solution of different concentrations (50, 100, 150, 200,300, 400, 500 μg/L) at pH value of 6.0 at 26 ± 2^0C. A series of such conical flasks were shaken for 80 min with Salvadora persica and Azadirachta indica ash at a speed of 100 rpm. Samples will be then agitated and filtered. The filtrates will be analyzed as mentioned before.

4. Results and Discussion

4.1. Effect Of Adsorbent Dosage

The adsorbent doses were varied from 0.5 g to 6 g. It is observed that the removal of metal ion increased with the increase in dosage of all the two tree barks studied attaining a maximum at 3 g of bark dosage. Obviously higher dose of adsorbent results in higher surface area providing greater number of binding sites for the metal ions.

4.2. Effect Of PH

pH is the key factor for the control of the adsorption of metal ions on the adsorbent. The effect of pH on removal of arsenic is shown in Fig 2.The study done in the pH range of 2 to 11. It is found that the adsorption of arsenic ion gradually increases as the initial pH of the solution is raised from 2 to 6. The maximum removal of arsenic in the case of the two tree barks viz., Salvadora Persica and Neem was found to be 92% and 86%, respectively, all at pH 6. Hence pH of the arsenic solution is maintained at 6 for further study.

4.3. Effect Of Contact Time

Percentage removal was recorded at contact time of 20 min to 240 min. The results are shown in Fig 3. Evidently more than 70 % arsenic removal in the case of all the two barks occurred within 20 min showing that initially the rate of uptake of arsenic is very fast and gradually increases attaining a steady value after reaching the equilibrium at about 80 min. Hence 80 min contact time was fixed for further study.

4.4. Effect Of Initial Concentration Of Arsenic

Experiments were performed by taking different initial concentrations of arsenic solution (10 ppb to 50 ppb) at pH 6 for a contact time of 60 and 80 min, taking 3 g of tree bark powder as bio adsorbent.The results (Fig4) show that percentage removal of arsenic ions decreased with increasing initial concentration in the case of all the three tree barks. This is because the adsorbtion sites become more saturated as the metal ion concentration increases.

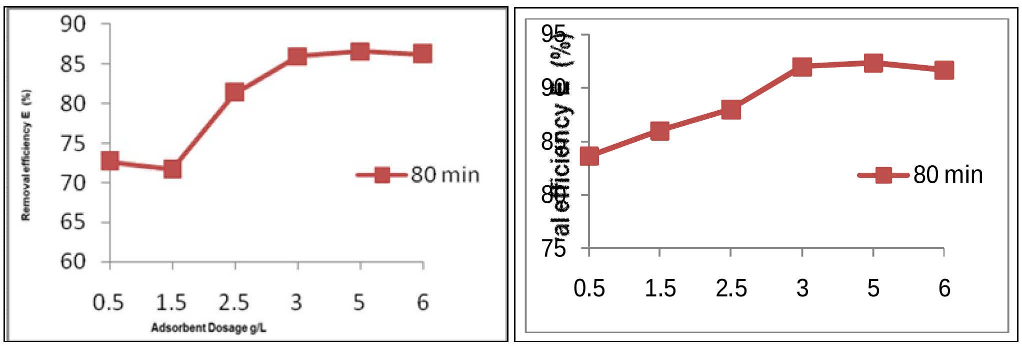

Figure 1: Effect of Adsorbent Dose on As(III) Removal
(The Initial As(III) Concentration =0.3 mg/L, pH = 6 and Contact Time of 60 and 80 min)

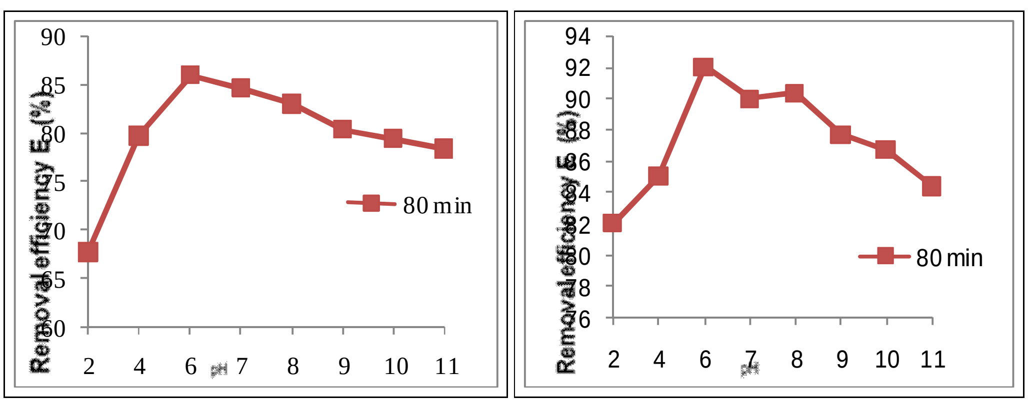

Figure 2: Effect of pH for the Adsorption of As(III) onto Azadirachta Indica and Salvadora persica Stem Ash
(The Initial As(III) Initial Concentration =0.03 mg/L, AdsorbentDose = 3 g/L and Contact Time = 60 Min)

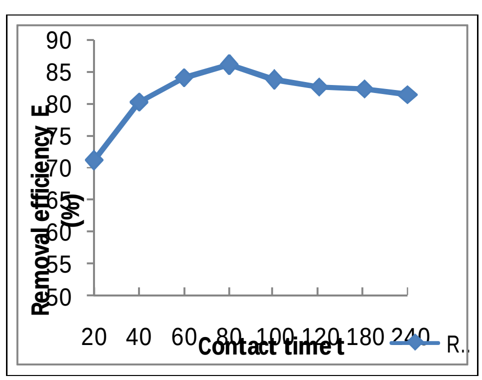

Figure 3:Effect of Contact Time for the Adsorption of As(III) onto Azadirachta Indica
and Salvadora persica Stem Ash (The Initial As(III) Concentration = 0.03 mg /L, pH = 6 and Adsorbent Dose = 3 g/L)

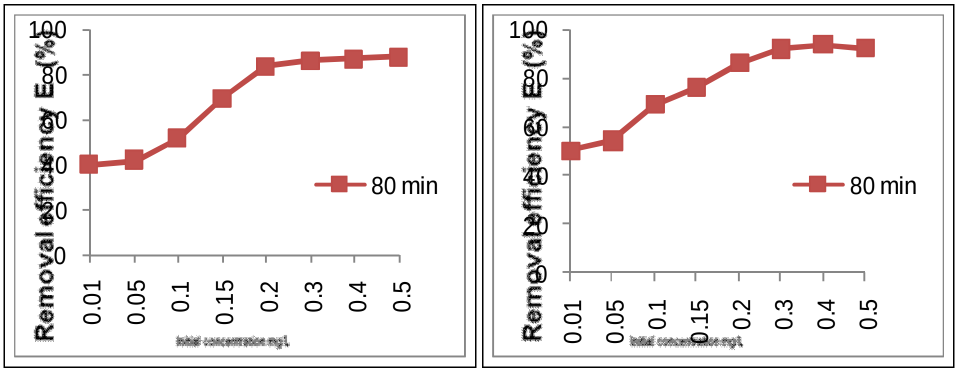

Figure 4: Effect of initial As(III) concentration for the adsorption of As(III) onto adsorbent in optimum condition (adsorbent dose =3 g/L, pH = 6 and contact time 60 and80 min for ash at 300◦C).

4.5. Adsorption Isotherm

A mathematical expression (graphical representation) that relates that amount of the gas adsorbed on the adsorbenont at constant temperature and the equilibrium pressure is called an adsorption isotherm. The isotherm provides a relationship between the concentration of As(III) in solution and the amount of As(III) adsorbed on the solid phase when both phases are in equilibrium.

5. Langmuir Isotherm

The Langmuir isotherm was developed by Irving Langmuir in 1916. The Langmuir isotherm, which is a model used to understand adsorption under a variety of circumstances is not used in day to day operation of the plant. Instead the calculation might be used to determine whether it would be economical to begin adding natural adsorbent to the water to remove one known contaminant. Alternatively the Langmuir isotherm can be used on a variety of types of natural adsorbent to determine which one would be most effective for dealing with a known contaminant.

The Langmuir isotherm is given below:

$$\frac{X}{M} = \frac{a\,b\,C_e}{1 + a\,C_e}$$

Where:

- X = Concentration of pollutant adsorbed mg/L = C_0 – Ce.
- M = Adsorbent concentration mg/L
- Ce = Equilibrium concentration mg/L
- a = constant (determined graphically)
- b = constant (determined graphically)

Alternatively, the equation can be manipulated to linear form, as shown below.

$$\frac{1}{X/M} = \frac{1}{ab} \times \frac{1}{Ce} + \frac{1}{b}$$

If familiar with algebra, this form will shows that "1/(X/M)" (or simply "M/X") is the y-value and "1/C_e" is the x-value when graphed. The value for "1/ab" is the slope and the value for "1/b" is the y-intercept.

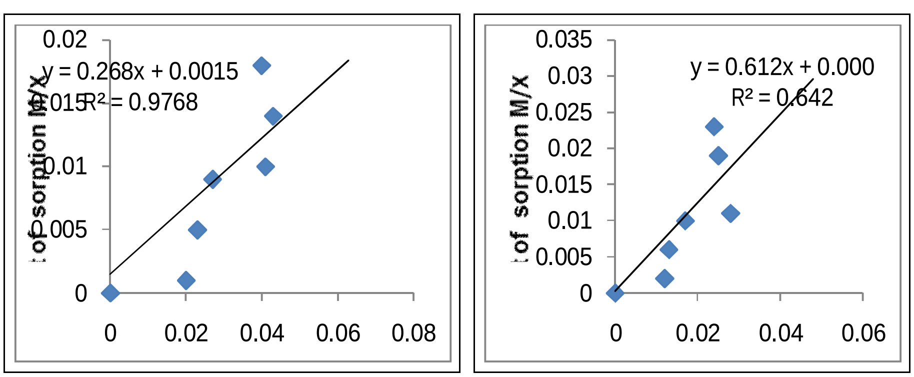

Figure 5: Langmuir Isotherm For Adsorption Of As(III) Onto Salvadora Persica Stem Ash Of Adsorbent Dosage

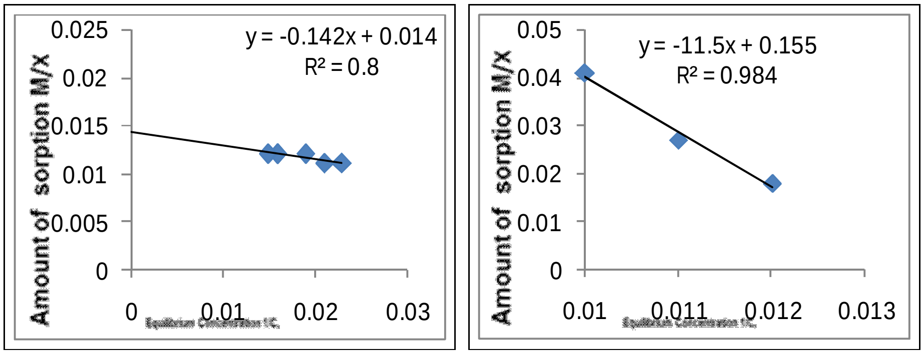

Figure 6: Langmuir Isotherm For Adsorption Of As(III) Onto Azadrichta indica and Salvadora Persica Stem Ash Of pH

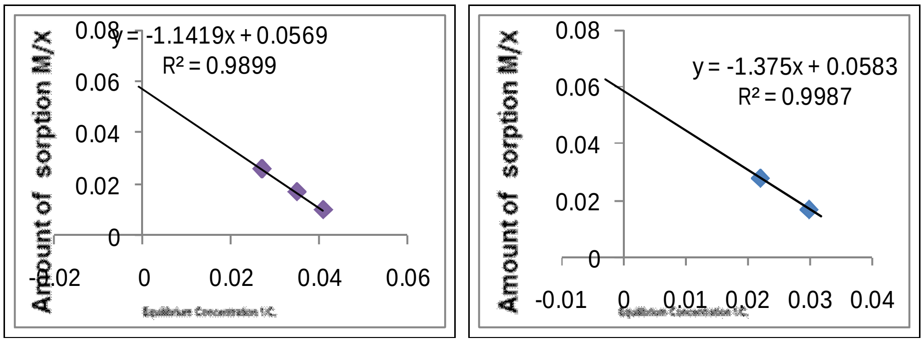

Figure 7: Langmuir Isotherm For Adsorption Of As(III)
Onto Azadrichta indica and Salvadora Persica Stem Ash Of Adsorbent Dosage

6. Freundlich Isotherm

Herbert Max Finley Freundlich a German physical chemist, presented an empirical bisorption isotherm for non-ideal system in 1906. The Freundlich isotherm is the earliest known relationship describing the applicability of heterogeneous surface energy in the bisorption process.

The empirical Freundlich equation is

$q_e = X/M = K C_e^{1/n}$

This can be rearranged and linearized as

$\text{Log}(X/M) = \log k + 1/n \log Ce$

Where

- X = concentration of pollutant adsorbed, mg/L = $C_0 - C_e$
- C_0 = Initial Concentration mg/L
- C = Equilibrium Concentration mg/L
- q_e = Amount of Adsorption mg/g
- V = Volume of Solution L
- M = Amount of Adsorbent g
- K = Constant (determined graphically)
- n = Constant (determined graphically).

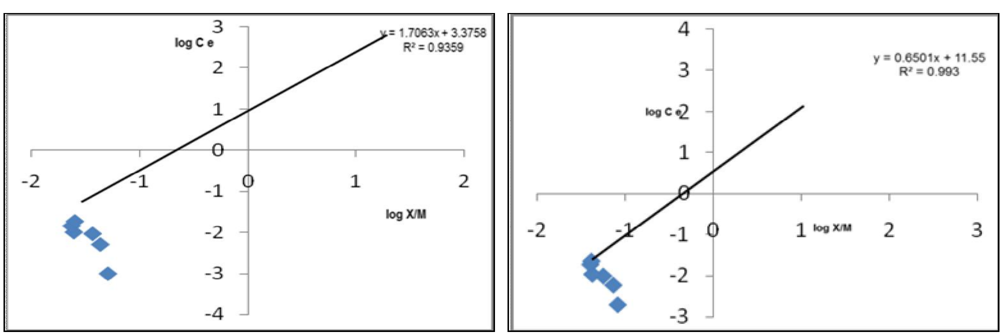

Figure 8:Freundlich Isotherm For Adsorption Of As(III)
Onto Azadrichta indica and Salvadora Persica Stem Ash Of Adsorbent Dosage

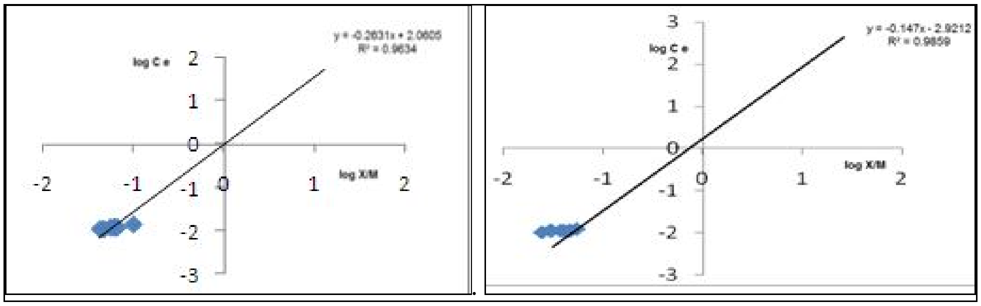

Figure 9: Freundlich Isotherm For Adsorption Of As(III) Onto Azadrichta indica and Salvadora Persica Stem Ash Of pH

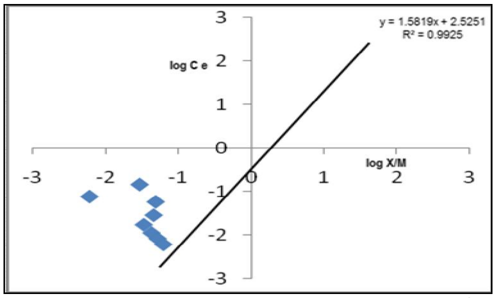

Figure 10: Freundlich Isotherm For Adsorption Of As(III)
Onto Azadrichta Indica and Salvadora persicaStem Ash For Different Initial Concentration

7. Seperation Factor R^2

Value of 'R^2' indicates the shape of isotherm

R value	Type of isotherm
R>1	Unfavorable
R=1	Linear
R<1	Favorable

Freundlich and Langmuir isotherm data for arsenic (III) a onto adsorbents are given in Table 2 and graphically shown in above Figures Comparing the correlation coefficient values of Freundlich isotherm with those of Langmuir isotherm. As mentioned above kis the equilibrium constant indicative of adsorption capacity and higher k means that the adsorption capacity is higher. Similarly parameter "b" is a function of the strength of adsorption; larger "b" means that the adsorption bond is stronger. It is clear that Langmuir isotherm fits better than Freundlich isotherm (b >k).

Parameters	Langmuir isotherm			Freundlich isotherm		
Azadrichta Indica	A	B	R^2	K	1/n	R^2
Adsorbent Dosage	0.04	50.00	0.9982	0.35	0.566	0.9930
Ph	0.03	63.69	0.8780	0.297	0.352	0.9634
Initial Concentration	0.04	17.15	0.9987	0.396	0.423	0.9925

Parameters	Langmuir isotherm			Freundlich isotherm		
Salvadora Persica	A	B	R^2	K	1/n	R^2
Adsorbent Dosage	0.04	66.66	0.9768	0.408	0.423	0.9359
Ph	0.03	17.57	0.9845	0.34	0.369	0.9859
Initial Concentration	0.05	18.11	0.9899	0.369	0.582	0.9459

Table 2: Pertinent Parameters of the Adsorption Isotherm Equations at 25 ± 2°C.

8. Regeneration of the Spent Adsorbent

The regeneration of the spent adsorbent was done. The spent adsorbent was shaked in 0.1 M NaOH at 22^0C for 4 hours. The removal efficiency of arsenic As(III) was decreased to 50% for 1g/L.

9. Conclusion

- The present work is carried out using different tree bark powder viz., Salvadora persica and Azadrichta indica as biosorbents which are found to be quite effective for the adsorption of arsenic from aqueous solutions.
- The effects of process parameters like pH, contact time, initial concentration and adsorbent concentration on equilibrium were studied.

- Of the two tree barks studied maximum removal of arsenic took place in the case of Salvadora persica tree bark followed by azadrichta indica tree bark in that order.

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