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A COMPARATIVE STUDY OF ARSENIC REMOVAL FROM SYNTHETIC SOLUTION USING ACTIVATED RED MUD (ARM) AND ACTIVATED FLY ASH (AFA) AS AN ADSORBENT.

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ABSTRACT:
Activated Red Mud (ARM) and Fly ash have been used as adsorbents for the removal of As (III) at room temperature. Various parameters such as pH, initial concentration of adsorbate, settling time, contact time and adsorbent dose were studied. The studied showed that at pH 9.7(alkaline condition) the removal of arsenic was effective. The process of arsenic adsorption follows a first –order rate expression and obeys the Langmuir's and Freundlich isotherms. Activated red Mud (ARM) has been observed to have greater adsorptive capacity than flyash.
KEYWORDS : Red Mud, Fly ash, arsenic removal, adsorption, adsorption isotherm.

INTRODUCTION:

Arsenic and its compound are extensively used in metallurgy, agriculture, forestry, electronics, pharmaceuticals, glassware, ceramic and dye industry, etc. Arsenic, being toxic pollutants, is introduced into the environment through weathering of rocks and mine tailing, industrial waste discharges, fertilizers, smelting of metals and burning of fossil fuels. The presence of arsenic in water causes toxic and carcinogenic effects on human beings. It has been reported that long-term uptake of arsenic contaminated potable water has produced gastrointestinal, skin, liver, and nerve tissue injuries. The toxicity of arsenic mainly depends upon on its oxidation state and trivalent arsenic has been reported to be more toxic than pentavalent arsenic. The presence of arsenic in potable water has been restricted to 0.05mg/l **(1).**

Arsenic removal from water can be done by various methods like precipitation, coagulation, ion exchange, etc. Among various available methods, adsorption appears to be most economical and effective treatment method. Activated carbon is the most efficient adsorbent for the removal of toxic metals like arsenic from water and waste water but its high cost restricts the use of activated carbon. Therefore, there is an urgent need to search alternate economically viable adsorbent materials. Various studies have been carried out in search of suitable adsorbents **(2-5).**

In the present study the flyash, a waste from Thermal Power Plant has been used as an adsorbent for the removal of arsenic from spiked or synthetic water prepared in the laboratory.

MATERIAL AND METHODS

All the reagents were prepared in double distilled or de-ionized water using analytical grade chemicals. The pH of the solution was adjusted with0.05M HNO_3 and NaOH.

Preparation of spike or synthetic solution: All chemicals used were of Analytical Grade.

Arsenic solution of 1000ppm: Dissolve 1.0gm of arsenic metal in 20ml 6N HNO_3 and dilute to 1 litre to obtain 1000ppm or 1000mg/l.

Red Mud: Red Mud is a by-product in the manufacture of alumina from bauxite by the Baeyer process. Red Mud used in present study was procured from INDALCO (Indian Aluminium Company) Belgaum, Karnataka State, India. This Red Mud was activated by the procedure described by Pratt et.al (6).The surface area of Red Mud was calculated by BET method. The surface structure of the Activated Red Mud (ARM) was observed by

Scanning Electron Microscope (SEM) (7). Compositions of red mud from different places are nearly the same and variation found is minimal. It consists mainly of different forms of iron and aluminum oxide minerals, calcium and sodium aluminum silicates, various titanium compounds, etc. The chemical composition of the Red Mud shown in **Table: 1**

Flyash: Flyash was also used as an adsorbent. It was collected from Koradi Thermal Power Station, Nagpur (Maharashtra).In India, about 30million tones of flyash are produced annually by the power plants. The proper disposal of flyash is a serious problem. The chemical composition of the Flyash shown in **Table: 2**

Chemically, flyash is an amorphous ferro-alumino-silicate. Silica and alumina are the major constituents of flyash. Besides, it contains,Fe_2O_3,CaO, MgO,etc. An empirical formula of flyash has also been worked out (8) as:

RESULTS AND DISCUSSIONS

Batch Adsorption Experiment: Adsorption of Arsenic metals.

Known concentration of arsenic solutions (500mg/l) were prepared and pH was adjusted to 6. 100ml solution was taken into stoppered glass bottle containing 1gm of adsorbent. The bottles were then shaken at room temperature using shaking machine. Blank solution was also shaken without adsorbent and the concentration was determined, which was taken as initial concentration.

Effect of contact time: The removal efficiency for arsenic was studied at pH 6, adsorbent dose: 1gm/100ml with initial concentration 500mg/l and settling time 4 hours. **Figure-1** illustrates the time in hours against the removal in percentage. It is observed that highest percent removal was achieved at 3 hours**.(Table 3&4).**The highest percentage of removal of arsenic by ARM and AFA was found to be 63% and 43.26% . At 3 hours contact time equilibrium was nearly established at a given pH and adsorbent dose. For arsenic

The uptake of adsorbate species is rapid in the initial stages of the contact time and gradually become slow near the equilibrium. This is obvious from the fact that large number surface sites are available for adsorption at the initial stages and after a lapse of time, the remaining surface sites are difficult to occupy because of repulsion between the solute molecules of the solid and bulk phase (2).

Effect of settling time: In order to study the effect of settling time, adsorbent dose, pH, initial concentration and contact time were the values 1gm/100ml, 6, 500mg/l and 3 hours respectively. The results are tabulated in **Table 5&6.**Settling time varied from 4 hours to 24 hours for the adsorbents i.e. ARM &AFA. The percentage of removal was found to be highest at 24 hours **(Figure-2).**Hence, in view of the findings the settling time was kept for 24 hours.

Effect of pH: The adsorption of arsenic metals by ARM & AFA was studied at different pH values to determine the optimum pH range for their removal. The results are tabulated in **Table-7 & 8** and also presented in **figure 3.**

The percentage of adsorption increases with the increase in pH up to certain range in all cases and the n decreases or nearly remains constant with further increase in pH. The maximum removal of arsenic was recorded at pH 6 and 5 when ARM and AFA was used as adsorbent materials. The highest removal i.e.83% of arsenic was observed when ARM was used as adsorbent materials **(Table-9).**

Adsorption isotherm:

The amount of metal ion adsorption increases with the increased adsorbent concentration where as it decreases with increase in adsorbate concentration indicating that adsorption depends upon the availability of binding sites for metal ions. In order to determine the adsorption capacity of the adsorbent, the equilibrium data for the adsorption of metal ions were analyzed in the light of Freundlich Adsorption Isotherm model.

$x/m = K.C_o^{1/n}$

or

$\log x/m = \log K + 1/n \log C_o$

where x/m is the amount of adsorbate (metal ions per gram of adsorbent), C_o is the equilibrium of metal ions in solution after the adsorption equilibrium is reached, k and n are constant known respectively as adsorption capacity and reciprocal adsorption intensity(8,9).

The log x/m against log C_o was plotted for different initial concentration arsenic metal while maintaining adsorbent doses at constant level (figure) represent metal ions adsorb per unit weight of adsorbent x/m as functions of equilibrium concentration (C_o).The adsorption capacities were directly obtained from these figures.

Linearity of the plot shows that the adsorption on the adsorbent closely obeys Freundlich's equation. With values of k and n, the actual forms of Freundlich equation for the arsenic metal under investigation are shown in **Table-8** which indicates that slope values of ARM and AFA are comparable for each other suggesting identical adsorption processes were occurring on the surface of both the adsorbents.

CONCLUSION:

In the present study it has been observed that the waste materials under investigation once brought in suitable form (activated) can be used as adsorbents for the removal of arsenic metal ions from synthetic water solution. It is found that these adsorbents have high potential for the removal of arsenic metal ions. The phenomenon of adsorption using ARM and AFA found to be pH dependent. In this study it has been found that Activated Red Mud (ARM) is a better adsorbent with greater adsorptive capacity and higher adsorption potential than that of Activated Fly Ash (AFA).

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Table-1:Chemical composition of the Red Mud

S.No.	Constituent	% (w/w)
1.	Fe_2O_3	33
2.	Al_2O_3	23
3.	TiO_2	12
4.	SiO_2	8
5.	Na_2O	6
6.	CaO	2
7.	P_2O_5	0.47
8.	V_2O_5	0.04
9.	CO_2	2.09
10.	S	0.09
11.	L.O.I (900^{0}C)	8.25

Table-2:Chemical composition of the Flyash

S.No.	Constituent	% (w/w)
1.	SiO	59.00
2.	Al_2O_3	27.70
3.	Fe_2O_3	07.40
4.	CaO	02.00
5.	MgO	02.00

Table-3: Effect of contact time on removal of Arsenic by ARM.

Adsorbent dose : 1gm/100ml pH : 6
Initial concentration : 500mg/1 Settling time : 4 hours

S.No.	Contact time (Hrs)	Remaining Conc. (mg/l)	Amount adsorbed (mg/l)	% Removal
1.	1.0	243	257	51.4
2.	1.5	237	263	52.6
3.	2.0	225	275	55.0
4.	2.5	205	295	59.0
5.	3.0	105	315	63.0
6.	3.5	180	320	64.0
7.	4.0	179	321	64.0

Table-4: Effect of contact time on removal of Arsenic by AFA.

Adsorbent dose : 1gm/100ml pH : 6
Initial concentration : 500mg/1 Settling time : 4 hours

S.No.	Contact time (Hrs)	Remaining Conc. (mg/l)	Amount adsorbed (mg/l)	% Removal
1.	1.0	372.15	127.85	25.57
2.	1.5	341.75	158.25	31.65
3.	2.0	313.55	186.45	37.29
4.	2.5	299.20	200.80	40.16
5.	3.0	283.70	216.30	43.26
6.	3.5	280.35	219.65	43.93
7.	4.0	279.15	220.85	44.17

Table-5: Effect of settling time on removal of Arsenic by ARM.

Adsorbent dose : 1gm/100ml pH : 6
Initial concentration : 500mg/1 Contact time : 3 hours

S.No.	Settling time (Hrs)	Remaining Conc. (mg/l)	Amount adsorbed (mg/l)	% Removal
1.	4.0	130.00	370.00	52.74
2.	8.0	197.60	302.40	60.48
3.	12.0	138.05	361.95	72.39
4.	24.0	80.55	419.45	83.89

Table-6: Effect of settling time on removal of Arsenic by AFA.

Adsorbent dose : 1gm/100ml pH : 6

Initial concentration : 500mg/l Contact time : 3 hours

S.No.	**Settling time (Hrs)**	**Remaining Conc. (mg/l)**	**Amount adsorbed (mg/l)**	**% Removal**
1.	4.0	290.20	209.80	41.96
2.	8.0	256.25	243.75	48.75
3.	12.0	219.15	280.85	56.17
4.	24.0	182.30	317.70	63.54

Table-7: Effect of pH on removal of Arsenic by ARM.

Adsorbent dose : 1gm/100ml Settling time : 24Hours

Initial concentration : 500mg/l Contact time : 3 hours

S.No.	**pH**	**Remaining Conc. (mg/l)**	**Amount adsorbed (mg/l)**	**% Removal**
1.	2	312.95	187.05	37.41
2.	3	253.35	246.65	49.33
3.	4	191.50	308.50	61.70
4.	5	108.05	391.95	78.39
5.	6	87.14	412.60	82.52
6.	7	76.05	423.95	84.79
7.	8	74.25	425.75	85.15

Table-:8 Effect of pH on removal of Arsenic by AFA.

Adsorbent dose : 1gm/100ml Settling time : 24Hours

Initial concentration : 500mg/l Contact time : 3 hours

S.No.	**pH**	**Remaining Conc. (mg/l)**	**Amount adsorbed (mg/l)**	**% Removal**
1.	2	344.10	155.90	31.18
2.	3	296.90	203.10	40.62
3.	4	203.55	296.45	59.29
4.	5	187.35	312.65	62.53
5.	6	187.75	312.25	62.45
6.	7	190.75	309.25	61.85
7.	8	187.25	312.75	62.55

Table-9: Maximum removal of arsenic at optimized pH.

S.No.	Adsorbent	pH	Hightest percent Removal
1.	ARM	6	82.52
2.	AFY	5	62.53

Table-8: Freundlich equation for arsenic metal.

S.No.	Metal ion	Adsorbent	Actual form of Freundlich equation
1.	Arsenic	ARM	$\log x/m = \log (1.10) + 0.1785\ 1/n \log C_o$
2.	Arsenic	AFA	$\log x/m = \log (1.09) + 0.1935\ 1/n \log C_o$

Fig. 1. Effect of contact time on removal of Arsenic by ARM and AFA

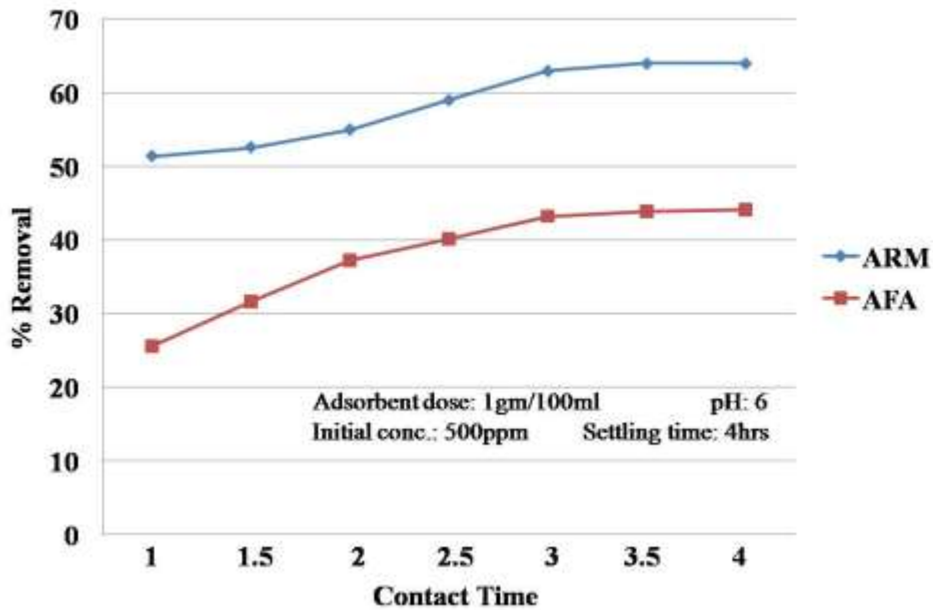

Fig. 2. Effect of settling time on removal of Arsenic by ARM and AFA

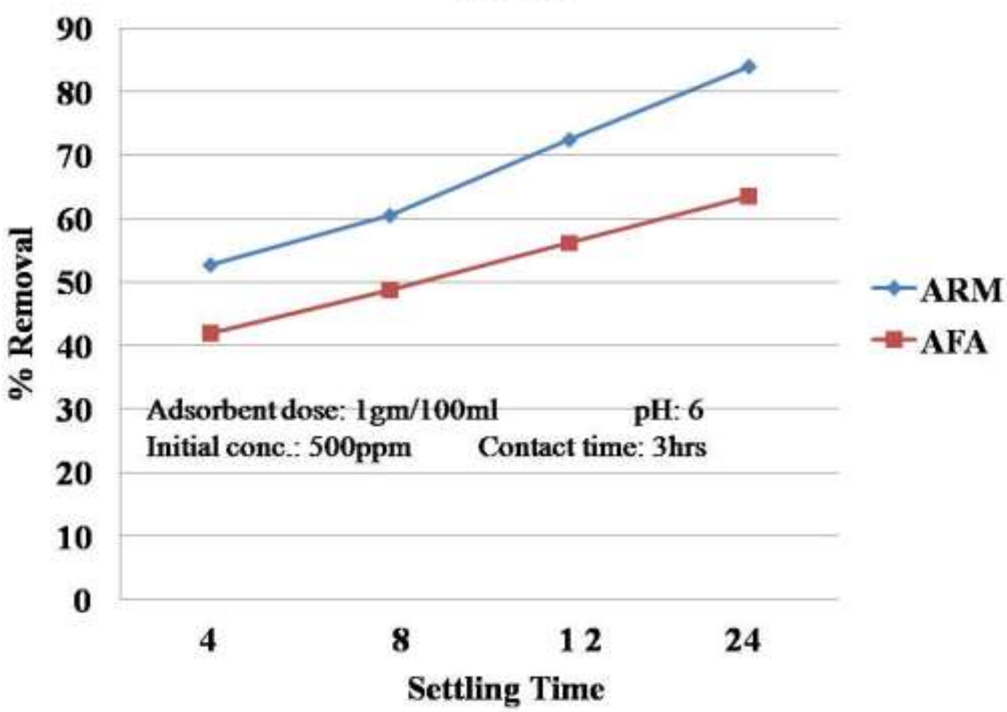

Fig. 3. Effect of pH on removal of Arsenic by ARM and AFA